of BI_3 with excess B_6H_{10} has also been found to yield $B_{13}H_{19}$ in up to 40% yield. Although mechanistically puzzling, this latter reaction constitutes the best currently available procedure for the preparation of $B_{13}H_{19}$. Though there is no doubt that a complex forms between B_6H_{10} and B_2Cl_4, nothing but decomposition products have been isolated at room temperature, and low-temperature investigations were hindered by solubility problems. Perhalogenation of the B_6H_{10} framework by an excess of the strongly Lewis acidic B_2Cl_4 may take place at room temperature, but $B_{10}H_{14}$ is the only stable isolated product from a reaction carried out in excess B_6H_{10}.

An interesting sidelight is the fact that the trialkylboranes $(CH_3)_3B$[20] and $(C_2H_5)_3B$ yield no evidence for complexation, whereas the trialkylaluminum species not only complex but polyalkylate the B_6H_{10}. Neither group of reactions is of synthetic value, however, for a reaction between the boranes and B_6H_{10} cannot be started and the reaction between B_6H_{10} and $(CH_3)_3Al$ or $(C_2H_5)_3Al$ cannot be stopped at intermediates. The only material exhibiting a ^{11}B NMR spectrum consistent with what would be expected for an adduct is the complex of $(i\text{-}C_4H_9)_3Al$ with B_6H_{10}. Apparently either triisobutylaluminum is either too bulky a Lewis acid to transfer an alkyl group or the electron-donating butyl groups neutralize the electropositive character of the aluminum atom enough so that the $(i\text{-}C_4H_9)_3Al{\cdot}B_6H_{10}$ complex is stable in excess triisobutylaluminum.

Reactivity of Hexaborane(10) in Comparison with Its Derivatives. Lewis basicity decreases as one procedes through the series $CH_3B_6H_9 > B_6H_{10} > IB_6H_9 > BrB_6H_9 > ClB_6H_9$, as determined by the rate and extent of reaction between these compounds and the boron trihalides and by the reactions with the borane Lewis acids B_3H_7 and B_8H_{12}. This agrees with the predicted availability of electron density at the B–B bond in these hexaborane derivatives. It also is parallel to the order of Bronsted basicity of hexaborane and its basal methylated derivative observed by Shore et al.[3]

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Registry No. B_6H_{10}, 23777-80-2; BCl_3, 10294-34-5; BBr_3, 10294-33-4; BI_3, 13517-10-7; BrB_6H_9, 50545-82-9; IB_6H_9, 75700-47-9; ClB_6H_9, 75700-48-0; B_2Cl_4, 13701-67-2; $(CH_3)_3Al$, 75-24-1; $(C_2H_5)_3Al$, 97-93-8; $(i\text{-}C_4H_9)_3Al$, 100-99-2; $I_2B_6H_8$, 75700-69-5; $CH_3B_6H_9$, 36863-02-2; $B_3H_7{\cdot}THF$, 52842-96-3; $B_6H_{10}{\cdot}(i\text{-}C_4H_9)_3Al$, 75700-49-1; $B_{13}H_{19}$, 43093-20-5; KB_6H_9, 12447-66-4; Cl_2, 7782-50-5.

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[20] This lack of complexation was observed in the reaction of $(CH_3)_3Al$ with B_6H_{10}, where $(CH_3)_3B$ was a major product of the reaction.

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Kinetics of Formation of (Thiourea)pentacyanoferrate(II) Complexes in Aqueous Perchlorate Media

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The kinetics of formation of complexes of the type $LFe(CN)_5^{3-}$ (L = thiourea and N-substituted derivatives) have been studied over the pH range 2.5–10. Second-order substitution rate constants show a hydrogen ion dependence, and at 25 °C, $k_0 = (k_a[H^+] + k_bK_a)/([H^+] + K_a)$, where $k_a \approx 1\ M^{-1}\ s^{-1}$ is the rate constant for the reaction of $HFe(CN)_5OH_2^{2-}$ with thioureas and k_b ($\sim$186–240 $M^{-1}\ s^{-1}$) governs the corresponding reactions of $Fe(CN)_5OH_2^{3-}$. Activation parameters have been measured for k_b and are similar to those for reaction of other uncharged ligands. The data show some differences at high pH from a previous study, there being no decrease in rate at pH >6. Comparisons are made of the dissociation rates of S- and N-bonded complexes.

In a previous paper,[1] we reported the results of a kinetic investigation of the substitution reactions of pentacyanaquoferrate(II) with thiourea and N-substituted derivatives. The dependence of the rates of substitution on acidity was attributed to three pH-related iron(II) species: $HFe(CN)_5OH_2^{2-}$, $Fe(CN)_5OH_2^{3-}$, and $Fe(CN)_5OH^{4-}$. The protonated aquo ion ($K_a = 2.35 \times 10^{-3}$ M)[2] was found to be much less reactive ($k_{25\,°C} \approx 2\ M^{-1}\ s^{-1}$) than the aquo form ($k_{25\,°C} \approx 200\ M^{-1}\ s^{-1}$), a difference which has also been observed in the pH-dependent reactions of $Fe(CN)_5OH_2^{3-}$ with *N*-methylpyrazinium ion.[2] At high pHs (>8), however, we attributed an apparent decrease in the observed reaction rate to a slower substitution process involving the hydroxy form. Other studies[3] with a number of ligands have reported essentially no change in the rates with acidity in the range pH 6–12. As was indicated earlier,[4] our observations are probably attributable to the presence of small (nonanalytically detectable) amounts of a dimeric impurity resulting from our preparation procedure. Recently, studies have been made involving the dimeric ion and rates in the pH range under consideration are $\sim 10^2$ slower than those for the monomeric species.[5] In this paper we report the results of a further investigation of the reaction of pentacyanoaquoferrate(II) with thioureas.

Experimental Section

Solutions of pentacyanoaquoferrate(II) ion were prepared by dissolution of solid $Na_3[Fe(CN)_5NH_3]{\cdot}3H_2O$ in deoxygenated distilled water. Three samples of the complex were used. Those from Fisher Chemical and one prepared from sodium nitroprusside by the conventional method[6] were recrystallized several times from saturated ammonia at 0 °C. Some data points were derived with use of a preparation by Dr. A. G. Lappin. In all cases the observed rate constants agreed to within ±3%. With the low concentrations of iron(II) used ((2–4) $\times 10^{-5}$ M), substitution processes due to the

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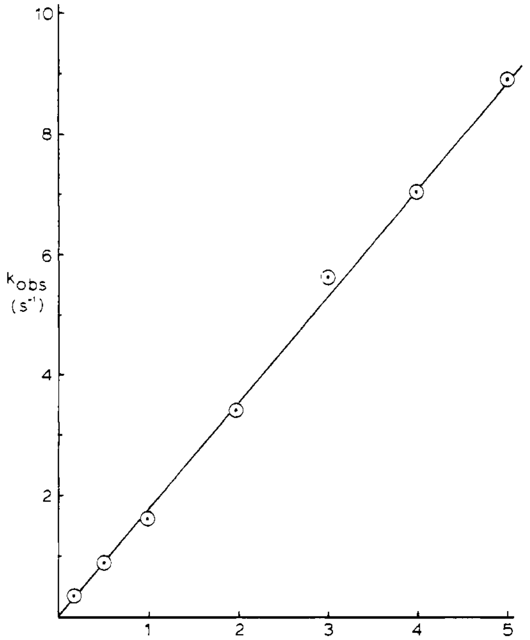

Figure 1. Plot of observed formation rate constants against thiourea concentration at 25 °C, pH 6.44, and $I = 0.50$ M ($NaClO_4$).

dimeric species were observed only at the higher temperatures with more aged solutions. The reaction of the monomer is readily distinguishable from the much slower processes involving the dimer.

Studies were made with use of a stopped-flow system described earlier,[7] the ionic strength of reactant solutions being maintained at 0.50 M with use of $NaClO_4$. The acidity of the reaction mixture was controlled by buffering (phthalate, phosphate, or borate buffers) of the ligand solutions. It has been shown that the stability of solutions of $Fe(CN)_5OH_2^{3-}$ decreases with increasing pH above pH 7.[3] Reactant iron(II) solutions were therefore maintained at pH ~5. In some instances, small amounts ($<10^{-4}$ M) of ascorbic acid were present to keep the iron in the reduced form. No detectable differences in rate were observed under these conditions.

The reactions were followed by monitoring the decrease in absorbance of $Fe(CN)_5OH_2^{3-}$ at 440 nm. All measurements were made under pseudo-first-order conditions with ligand in excess. Plots of ln $(A_\infty - A_t)$ against time derived from a PCM computer linked to the photomultiplier output were linear for at least 3 half-lives.

Results and Discussion

As observed previously, on reaction of pentacyanoferrate(II) species with thioureas (TU = thiourea, ATU = allylthiourea and DMTU = *N,N'*-dimethylthiourea), a rapid complex formation is observed with shift of λ_{max} in the visible region to 406 nm. Under the reaction conditions prevailing, [TU] ≫ [Fe(II)], the rate of formation is given by eq 1, where k_{obsd}

$$d[Fe(CN)_5TU^{3-}]/dt = k_{obsd}[Fe(CN)_5OH_2^{3-}] \qquad (1)$$

$= k_0$[TU]. The first-order dependence on ligand concentration is shown in Figure 1. Evidence for an intercept found previously[1] and suggestive of an equilibrium condition is considered to be an artifact of the solutions used. The finding of a strict overall second-order dependence on the rate is in keeping with those of other workers[3,8-11] and confirms that the thiourea complexes are thermodynamically more stable than suggested previously.[1] Kinetics consistent with eq 1 were found for all three ligands studied. Table I contains ligand concentration dependences for thiourea (several acidities), allylthiourea, and dimethylthiourea at 25 °C. The second-order rate constant, k_0, for thiourea at pH >6 (186 M^{-1} s^{-1}) may be compared with that of Davies[3] (153 ± 3 M^{-1} s^{-1}) measured at a higher ionic strength (1.0 M $NaClO_4$). There appears to be some dependence of rate on ionic strength. The formation rate constant of the Me_2SO complex has been found to be 240 M^{-1} s^{-1} at $I = 1.0$ M[9] and 345 M^{-1} s^{-1} at $I = 0.1$ M.[10] A similar situation obtains for isonicotinamide, where the rate constants are 296 M^{-1} s^{-1} ($I = 0.5$ M)[11] and 196 M^{-1}

Table I. Rate Constants for the Reaction of $Fe(CN)_5OH_2^{3-}$ with Thiourea Ligands[a]

pH	10^3[L], M	k_{obsd},[b] s^{-1}	k_1, M^{-1} s^{-1}
	Thiourea		
3.66	2.00	0.366	159 ± 4
	4.00	0.681	
	6.00	0.960	
	8.00	1.33	
6.44	2.00	0.408	181 ± 8
	5.00	0.805	
	10.0	1.62	
	20.0	3.40	
	30.0	5.69	
	40.0	7.06	
	50.0	8.97	
8.17	2.25	0.430	182 ± 4
	4.50	0.857	
	6.75	1.23	
	9.00	1.67	
	Allylthiourea		
6.58	2.00	0.391	192 ± 9
	5.00	0.857	
	10.0	1.99	
	15.0	2.86	
	20.0	3.83	
	Dimethylthiourea		
6.53	2.00	0.462	236 ± 7
	6.00	1.50	
	10.0	2.39	
	15.0	3.62	
	20.0	4.71	

[a] $T = 25.0$ °C; $I = 0.50$ M ($NaClO_4$). [b] ±4%.

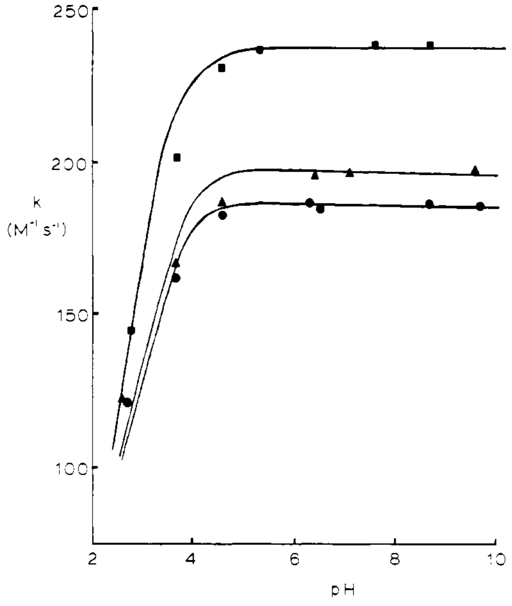

Figure 2. Variation in second-order rate constant as a function of pH ($T = 25$ °C): ■, dimethylthiourea; ▲, allylthiourea; ●, thiourea. The full lines are those calculated with use of the data in the text.

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Table II. pH Dependence of Substitution Rates[a]

pH	k_1, M^{-1} s^{-1}	pH	k_1, M^{-1} s^{-1}
	Thiourea		
2.73	120	6.23	185
3.65	161	6.55	184
4.70	182	8.65	186
5.57	189	9.70	185
	Allylthiourea		
2.65	118	6.58	192
3.65	165	7.20	195
4.70	183	9.65	196
	Dimethylthiourea		
2.80	144	5.35	235
3.65	201	7.62	238
4.66	231	8.58	239

[a] $T = 25$ °C; $I = 0.50$ M ($NaClO_4$).

Table III. Temperature Dependence of Substitution Rates

ligand	T, ±0.05 °C	k_1, M^{-1} s^{-1}	$\Delta H^\ddagger$,[a] kcal/mol	$\Delta S^\ddagger$,[a] cal/(deg·mol)
thiourea	12.6	56	15.7	5
	14.5	67		
	17.0	86		
	19.9	119		
	25.0	186		
	29.7	282		
allylthiourea	12.6	57	16.7	8
	14.5	72		
	19.9	112		
	21.0	143		
	25.0	196		
	28.5	283		
dimethylthiourea	12.6	75	15.5	4
	14.0	94		
	17.0	116		
	19.9	149		
	25.0	238		
	28.5	346		

[a] $\Delta H^\ddagger = \pm 0.5$ kcal/mol; $\Delta S^\ddagger = \pm 2$ cal/(deg·mol).

s^{-1} ($I = 1.0$ M)[3], respectively. The dependence of substitution rate constants, k_0, on pH is shown in Figure 2. As previously reported, there is a steep rise in complex formation rate between pH 2 and 5 owing to the greater reactivity of $Fe(CN)_5OH_2^{3-}$ over the protonated form $HFe(CN)_5OH_2^{2-}$. A mechanism consistent with the observations may be written as

$$HFe(CN)_5OH_2^{2-} + TU \xrightarrow{k_a} Fe(CN)_5TU^{3-} + H_3O^+ \qquad (2)$$

$$+H^+ \Big\updownarrow -H^+ (K_a)$$

$$Fe(CN)_5OH_2^{3-} + TU \xrightarrow{k_b} Fe(CN)_5TU^{3-} + H_2O \qquad (3)$$

so that

$$k_0 = (k_a[H^+] + k_bK_a)/([H^+] + K_a) \qquad (4)$$

From a knowledge of the dissociation constant for the protonated species[2] ($pK_a = 2.63 \pm 0.12$) it is possible to determine individual reaction pathways. The calculated profile for k_0 against pH is shown with the data in Figure 2, where $k_a \approx 1$ M^{-1} s^{-1}. This confirms our earlier finding of a very low rate of reaction of the protonated complex. A similar result has been found by Malin[2] in the reaction with *N*-methylpyrazinium ion where protonation of the pentacyanoaquoferrate(II) ion decreases the rate of reaction by a factor of at least 50. The pH dependence of substitution rates for the three substrates is presented in Table II, and rate constants at various temperatures and activation parameters are given in Table III.

The mechanism of formation of $[Fe(CN)_5L]^{n-}$ complexes has been considered as essentially dissociative in character. Support for this proposal comes from the lack of variation in k_0 values over a series of ligands (Table IV). The present data lend further weight to this view. The relatively small range of rate constants (186–240 M^{-1} s^{-1}) for the three thioureas studied may be compared with the rate for the (sulfur-bonded) dimethyl sulfoxide complex ($k_0 = 240$ M^{-1} s^{-1}).[9] We have also measured the rate of dissociation of the $Fe(CN)_5TU^{3-}$ complexes in the presence of pyridine.[1] For both formation and dissociation processes it appears that mechanism (5)–(7) is consistent with the data, where L is thiourea or

$$Fe(CN)_5OH_2^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(CN)_5^{3-} + H_2O \qquad (5)$$

$$Fe(CN)_5^{3-} + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe(CN)_5L^{3-} \qquad (6)$$

$$Fe(CN)_5^{3-} + py \xrightarrow{k_3} Fe(CN)_5py^{3-} \qquad (7)$$

N-substituted thioureas. In the formation reactions of $Fe(CN)_5L^{3-}$ where there is no added pyridine the observed rate constant may be expressed by eq 8 with assumption of

$$k_{obsd} = k_1k_2[L]/(k_{-1}[H_2O] + k_2[L]) \qquad (8)$$

steady-state conditions in $[Fe(CN)_5^{3-}]$. Since $k_{-1}[H_2O] \gg k_2[L]$, there is a first-order dependence on [L] and no limiting value of k_{obsd} is found at high thiourea concentrations (Figure 1).

In the case of the dissociation reactions of $Fe(CN)_5L^{3-}$ in the presence of pyridine the observed rate constant for the formation of $Fe(CN)_5py^{3-}$ may be expressed as eq 9 with

$$k_{obsd} = k_{-2}k_3[py]/(k_2[L] + k_3[py]) \qquad (9)$$

assumption of a steady state in $[Fe(CN)_5^{3-}]$. At high pyridine concentrations such that $k_3[py] \gg k_2[L]$ the rate constant reduces to k_{-2}. The dissociation rate constants and activation parameters are listed in Table IV for $Fe(CN)_5L$ complexes having a variety of ligand types. Whereas the formation rate constants are virtually independent of the nature of ligand L, the sulfur-bonded systems show somewhat higher rates of

Table IV. Kinetic and Activation Parameters for the Formulation and Dissociation Reactions of Various Pentacyanoferrate(II) Complexes

ligand	k_f, M^{-1} s^{-1}	$\Delta H_f^\ddagger$ [a]	$\Delta S_f^\ddagger$ [b]	10^3k_d, s^{-1}	$\Delta H_d^\ddagger$ [a]	$\Delta S_d^\ddagger$ [b]	ref
pyridine	365	16.1	7	1.10	24.8	11	8, 11
isonicotinamide	296	15.8	6	0.73	26.0	14	8, 11
pyrazine	380	15.4	5	0.42	26.4	14	8, 11
imidazole	240	15.2	3	1.33	24.3	10	10
histidine	320	15.4	5	5.3	25.2	11	10
dimethyl sulfoxide	240	15.4	4	0.075	26.5	11	9
thiourea	186	15.7	5	39.0	16.6	−9	c
allylthiourea	196	16.7	8	45.1	16.3	−10	c
dimethylthiourea	238	15.5	4	81.3	18.0	−3	c

[a] kcal/mol. [b] cal/(deg·mol). [c] This work and ref 1.

dissociation than those for N-bonded complexes.

Further studies using thiol ligands, where the reactivity of both RSH and RS^- species may be investigated in the high-pH range, are in progress.

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Registry No. $Fe(CN)_5OH_2^{3-}$, 18497-51-3; TU, 62-56-6; ATU, 109-57-9; DMTU, 534-13-4.

Contribution from the Departments of Chemistry, Faculty of Science, University of Sarajevo, Sarajevo, Yugoslavia, and University of Minnesota, Minneapolis, Minnesota 55455

Solvent Interchange of Pentaamminecobalt(III) Ions in Water–Acetonitrile and in Dimethyl Sulfoxide–Acetonitrile Media

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Solvent-interchange reaction rates have been determined for $[CO(NH_3)_5(NCCH_3)](ClO_4)_3$ in acetonitrile–water and in acetonitrile–dimethyl sulfoxide solvent mixtures. Ratios of reactants and products in equilibrium mixtures and first-order rate constants are reported. The rate constants k_A and k'_A for reaction of acetonitrile with the aquo and dimethyl sulfoxide complexes were strongly dependent on the mole fraction of acetonitrile in the solvent. The rate constants for the reverse reactions for loss of acetonitrile from the acetonitrile complex were only slightly dependent on the mole fraction of acetonitrile. One interpretation of the results is that the $Co(NH_3)_5^{3+}$ group in the activated complex of the I_d mechanism for solvent interchange does not undergo any significant real rotation or pseudorotation within its solvent cage. The activation enthalpy for water reacting with the acetonitrile complex was 26.5 ± 0.5 kcal mol^{-1}, that for acetonitrile reacting with the aquo complex was 28.7 ± 0.4 kcal mol^{-1}, that for acetonitrile reacting with the dimethyl sulfoxide complex was 27.0 ± 0.5 kcal mol^{-1}, and that for dimethyl sulfoxide reacting with the acetonitrile complex was 27.8 ± 0.5 kcal mol^{-1}.

The I_d (interchange with dissociative character) model has been accepted[2-5] for the mechanism of substitution reactions of $Co(NH_3)_5S^{3+}$ such as shown in reaction 1, where S is a

$$Co(NH_3)_5S^{3+} + Y \rightleftarrows Co(NH_3)_5Y^{3+} + S \qquad (1)$$

solvent molecule and Y is an anion, an uncharged ligand, or another solvent molecule. In this mechanism $Co(NH_3)_5S^{3+}$ first forms an encounter complex with Y, and then the encounter complex becomes activated, breaking the Co(III)–S bond and moving S to the solvent cage[4] around the five-coordinate $Co(NH_3)_5^{3+}$ group. The nucleophile Y must also be in this solvent cage if it is to be interchanged for S because $Co(NH_3)_5^{3+}$ does not exist sufficiently long to diffuse from this solvent cage and react with nucleophiles outside of the solvent cage; Langford[3] has appropriately described this reaction as "accidentally bimolecular". When Y is another S molecule (solvent exchange), the potential energy barrier can be qualitatively described as in Figure 1. The barrier top is essentially flat, as assumed in absolute rate theory, within the energy uncertainty arising from the short lifetime of the transition state. At the configuration designated by $X_1^{\ddagger}$ the Co(III)–S bond has been broken, at $X_2^{\ddagger}$ the leaving and entering S molecules are equivalent as required by the principle of microscopic reversibility, and at $X_3^{\ddagger}$ the Co(III)–*S bond has been broken in the reverse reaction. (Langford[4] has pointed out the lack of bonding in this mechanism between Co(III) and the entering group.) If the $Co(NH_3)_5^{3+}$ group can rotate or pseudorotate freely within its solvent cage before it is deactivated, it can fill the vacant first-coordination-shell site more or less statistically from among the properly oriented nucleophiles (all S molecules in solvent exchange) in the solvent cage. In this case, there will be many orientations of $Co(NH_3)_5^{3+}$ within the solvent cage, all with equal energies within the energy uncertainty, and there will be a barrier like that shown in Figure 1 for each orientation through which the system passes from breaking of the Co(III)–S bond to forming of the Co(III)–*S bond.

In a mixture of two solvents S and Y both of which can form bonds to Co(III) the solvated complex $Co(NH_3)_5S^{3+}\cdot S_s\cdot Y_y$, containing *s* S molecules and *y* Y molecules in the solvation shell, is the encounter complex. (There probably is a range of *s* and *y* values for any given bulk mole fraction of Y.) Activation of this complex and breaking of the bond between Co(III) and the inner-sphere S can occur. If there is free rotation or pseudorotation of $Co(NH_3)_5^{3+}$ within its solvent cage the vacant coordination site can be repositioned with respect to the solvent cage. When deactivation occurs, $Co(NH_3)_5^{3+}$ may combine (1) with the original S molecule (internal return), (2) with a different S molecule (solvent exchange) by passage through a configuration analogous to $X_3^{\ddagger}$ in Figure 1, or (3) with a Y molecule and pass through a configuration $X_4^{\ddagger}$ (not shown in Figure 1) on an unsymmetrical barrier for formation of $Co(NH_3)_5Y^{3+}$ from $Co(NH_3)_5S^{3+}$. Here we present some results consistent with the absence of such free rotation of $Co(NH_3)_5^{3+}$ with respect to the solvent cage in which it was formed.

Experimental Section

Materials. The compounds $[Co(NH_3)_5OH_2](ClO_4)_3$,[6] $[Co(NH_3)_5OSMe_2](ClO_4)_3\cdot 2H_2O$,[7] and $[Co(NH_3)_5(NCCH_3)](ClO_4)_3$[8] were prepared as described previously in the literature. The *p*-toluenesulfonic acid (PTSA) was obtained from Eastman Kodak Co. and was purified by recrystallization from ethanol. Dimethyl sulfoxide, Me_2SO, was obtained from Aldrich Chemical Co. and was purified by distillation under reduced pressure with the middle two-thirds fraction collected. Acetonitrile was obtained from Eastman Kodak Co. and was purified by distillation with the middle two-thirds fraction

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