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Contribution from the Department of Chemistry, University College, University of New South Wales,
Australian Defence Force Academy, Northcott Drive, Campbell, ACT, Australia 2600

Role of Ion Pairs in Anation Reactions of $(NH_3)_5CoX^{n+}$: Capture of the Thiocyanate Ion in Mixed-Anion Competition Studies

W. G. Jackson,* B. C. McGregor, and S. S. Jurisson

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The rates of hydrolysis of $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ and especially $[(NH_3)_5CoO_3SCF_3]^{2+}$ in SCN^-/SO_4^{2-} ($I = 3.1$ M) media are accelerated appreciably by SO_4^{2-}. This observation, which has precedent, is attributed to the formation of more reactive SO_4^{2-} ion pairs. Anion competition by both SO_4^{2-} and SCN^- is observed. Thiocyanate ion capture leads to both S- and N-bonded $[(NH_3)_5Co(SCN)]^{2+}$ products. The S-bonded/N-bonded isomer distribution is independent of $[SCN^-]$ and $[SO_4^{2-}]$, but the more remarkable result is the $[SO_4^{2-}]$ independence of the SCN^- competition ratio, $[(NH_3)_5Co(SCN)^{2+}]/[(NH_3)_5CoOH_2^{3+}][SCN^-]$. Thus, SCN^- competition depends linearly on $[SCN^-]$, as is usual, yet for each complex ion system studied more than 50% of the reaction proceeds via the SO_4^{2-} ion pairs above ~0.3 M SO_4^{2-}. It is shown that anions are not captured efficiently from either SO_4^{2-} or SCN^- ion pairs, and the mixed-anion competition results lead to the inescapable conclusion that product formation does not arise *directly* from preformed $[(NH_3)_5CoX]^{n+},SO_4^{2-}$ or $[(NH_3)_5CoX]^{n+},SCN^-$ ion pairs. Rather, the very short lived $[(NH_3)_5Co]^{3+}$ intermediate is proposed, and this captures SCN^-, SO_4^{2-}, and H_2O from an inherited ion atmosphere in a non-rate-determining step. This study casts doubt on the general validity of the widely accepted Eigen–Wilkins mechanism for metal ion anion-substitution reactions. This conclusion arises from the effective experimental separation of the rate-determining and product-determining steps using mixed-anion systems.

Introduction

Recent publications have highlighted the difficulties of distinguishing dissociative processes from limiting dissociative processes for the substitution reactions of octahedral cobalt(III) complexes.[1-7] The problem is one of ascertaining whether an intermediate of chemically significant lifetime is formed. Most experiments designed to explore this aspect of mechanism have involved reactions between cations and anions, and inter alia, there exist ambiguities in the interpretation of the results because of the inevitability of ion pairing. Some time ago we presented evidence demonstrating that preequilibrium ion-pair formation between $[(NH_3)_5CoX]^{n+}$ and Y^{m-} was *not* a requirement for the capture of Y^{m-} in the base-catalyzed hydrolysis reactions of $([NH_3)_5CoX]^{n+}$, carried out in the presence of excess Y^{m-} (which results in $[(NH_3)_5CoY]^{(3-m)+}$ along with $[(NH_3)_5CoOH]^{2+}$).[7] The formation of $[(NH_3)_5CoY]^{(3-m)+}$ was interpreted as arising from capture of Y^{m-} by a short-lived five-coordinate intermediate $[(NH_2)(NH_3)_4Co]^{2+}$. More recently in a study of SCN^- capture during the spontaneous aquation of $[(NH_3)_5CoX]$ for varied X, it was suggested that the long-standing distinction between spontaneous (dissociative) and induced aquation (limiting dissociative) was artificial and that all the data could be accommodated by a very short lived five-coordinate intermediate $[(NH_3)_5Co]^{3+}$, the lifetime of which depended upon its rate of generation.[8] In the present work we present further evidence in support of this view.

In particular, we report kinetic and anion competition data for the spontaneous aquation of some labile $[(NH_3)_5CoX]^{n+}$ species, carried out in SCN^-/SO_4^{2-} media at constant ionic strength for a range of $[SO_4^{2-}]$. These experiments were designed to examine the role of preformed ion pairs in the product-determining step(s) which yield $[(NH_3)_5CoOSO_3]^+$ and $[(NH_3)_5Co(SCN)]^{2+}$ along with $[(NH_3)_5CoOH_2]^{3+}$. Sulfate ion was chosen because it can exist in acid solution as a 2− anion and because of its ion-pairing capacity with 2+ and especially 3+ complex ions,[7] despite the relative high ionic strengths demanded by the anion competition experiments, and SCN^- because of its lower ion-pairing capcity yet the ability to compete successfully with water in the substitution process.[9] Moreover, SCN^- competition affords both $[(NH_3)_5CoSCN]^{2+}$ and $[(NH_3)_5CoNCS]^{2+}$, providing an additional handle on the product distributions, which are crucial to the interpretation of the results.[8-11] A method for the accurate determination of the individual species $[(NH_3)_5CoSCN]^{2+}$ and $[(NH_3)_5CoNCS]^{2+}$ at the low concentration levels expected has been recently reported.[10] Also, the typical 2+ and 3+ complexes $[(NH_3)_5CoO_3SCF_3]^{2+}$ and $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ were chosen as substrates for these competition experiments because they spontaneously aquate on time scales quite short[8] compared with those for subsequent reactions, in particular the S- to N-bonded rearrangement of $[(NH_3)_5CoSCN]^{2+}$ and the SCN^- and SO_4^{2-} anation of $[(NH_3)_5CoOH_2]^{3+}$.[11,12]

Experimental Section

Electronic absorption spectra (ϵ_λ, M^{-1} cm^{-1}; λ, nm) were recorded at 25 °C with use of a Cary 118C instrument. Proton NMR spectra were obtained on a Varian T60 instrument for Me_2SO-d_6 (Merck; 99.9% D) solutions at 35 °C. Ion-exchange resins used were Biorad Dowex 50WX2 (200–400 mesh; H^+ or Na^+ form) and SP-Sephadex C-25 (Pharmacia; Na^+ form). Other chemicals were AnalaR or an equivalent grade.

The complexes $[(NH_3)_5CoOSO_3]ClO_4{\cdot}H_2O$ (ϵ_{515}^{max} 63.9),[5,7] $[(NH_3)_5CoSCN]Cl_2{\cdot}5H_2O$ and $[(NH_3)_5CoSCN](ClO_4)_2$ (ϵ_{514}^{max} 74.8, ϵ_{288}^{max} 15 680), $[(NH_3)_5CoNCS]Cl_2$ and $[(NH_3)_5CoNCS](ClO_4)_2$ (ϵ_{498}^{max} 169, ϵ_{306}^{max} 1598),[8,9] and $[(NH_3)_5CoO_3SCF_3](ClO_4)_2$[13] were fresh batches used in concurrent work. Absorption spectra (H_2O, pH 3), measured in triplicate, were identical with those documented. The synthesis and characterization of the fluoroacetamide complex,[14] prepared from the reaction between $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$ and FCH_2CONH_2 in Me_2CO, is given elsewhere. Both the O- and N-bonded amide complexes have been obtained;[14,15] the triflate route gives exclusively the O-bonded iso-

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mer. The salts $[(NH_3)_5CoOC(NH_2)CH_2F]_2S_2O_6{\cdot}3H_2O$ and $[(NH_3)_5CoOC(NH_2)CH_2F](ClO_4)_2$ were characterized for the present work. Their vis/UV spectra were identical, and the ^1H NMR spectrum of the ClO_4^- salt in Me_2SO-d_6 agreed with that determined for authentic O-bonded isomer (δ 3.83, cis-NH_3, 12 H; δ 2.72, trans-NH_3, 3 H; δ 7.31, NH, 1 H; δ 9.17, NH, 1 H; δ 4.70, $-CH_2F$, d, 2 H, J_{HF} = 46 Hz; Me_2SO-d_6, TMS).[14,15] All complexes analyzed satisfactorily and were shown by ion-exchange chromatography and ^1H NMR spectroscopy to be free of trace (<0.3%) impurities of other $[(NH_3)_5CoX]^{2+}$ species, $[(NH_3)_5CoOH_2]^{3+}$ in particular.

Kinetics. All reactions were followed spectrophotometrically on the Cary 118C instrument by using the in situ technique. To pre-temperature-equilibrated solvent (10 min) at 25.0 ± 0.1 °C, containing the appropriate mixture (pipet) of 3.10 M NaSCN (pH 4, $HClO_4$) and 1.00 M Na_2SO_4/0.100 M $NaHSO_4$ at I = 3.1 M, was added a judicious amount of solid complex $[(NH_3)_5CoO_3SCF_3](ClO_4)_2$ or $[(NH_3)_5CoOC(NH_2)CH_2F]_2S_2O_6{\cdot}3H_2O$. This was dissolved (<3 s) by rapid shaking, and measurements (D, t) commenced in the absorbance–time mode within 5 s. Reactions were followed at 580, 520, and/or 289 nm. Appreciable absorbance decreases (580, 520 nm) and increases (289 nm, SCN^- media) were observed. Reactions were followed to essential completion ($\geq 5t_{1/2}$), and clean first-order kinetics were observed. First-order rate constants were obtained by nonlinear least-squares analysis of the D–t data in the usual way by using KINCAL running on a Mac.[16] Results equivalent to good linear plots of $\ln|D-D_\infty|$ vs t over at least $3t_{1/2}$ were obtained. All runs were performed in quadruplicate, and no interference from the much slower subsequent reactions, SCN^- and SO_4^{2-} anation[11,12] of $[(NH_3)_5CoOH_2]^{3+}$ and S- to N-bonded isomerization[9] of $[(NH_3)_5CoSCN]^{2+}$, was experienced. This was clear from the wavelength independence of the k(obsd) values (see Results)—289 nm is especially sensitive to very small variations in $[(NH_3)_5CoSCN^{2+}]$.

Product Analysis. The reactions of $[(NH_3)_5CoO_3SCF_3](ClO_4)_2$ and $[(NH_3)_5CoOC(NH_2)CH_2F]_2(S_2O_6)_3{\cdot}H_2O$ (~300 mg) in the appropriate $NaSCN/Na_2SO_4/NaHSO_4$ mixture (25–50 mL) were allowed to proceed at 25.0 °C for 5 min or 5 h ($>10t_{1/2}$), respectively, and then quenched by dilution (to ~500 mL) with ice water. The reaction times were varied in some experiments (t = 5 min, 5 h for $CF_3SO_3^-$ (and 1.5, 2.5, and 5 h for FCH_2CONH_2) to check the (small) effect of subsequent reaction. The product mixtures were sorbed onto a column (15 × 3 cm) of Sephadex resin, washed (5 °C H_2O, pH 4), and eluted (NaCl, pH 3) to separate first $[(NH_3)_5CoOSO_3]^+$ (0.15 M), followed by $[(NH_3)_5CoNCS]^{2+}$ + $[(NH_3)_5CoSCN]^{2+}$, (0.25 M) and finally $[(NH_3)_5CoOH_2]^{3+}$ (1.0 M). The cobalt concentrations in the eluates of measured volume and the S- to N-isomer ratio for $[(NH_3)_5Co(SCN)]^{2+}$ were determined as previously.[8,10,11] Dowex resin (1 M KCl and 3 M HCl eluants)[7,18] was used to determine $[(NH_3)_5CoOSO_3]^+$, in separate experiments, since often it was not satisfactorily retained on Sephadex during the absorption process. All experiments were carried out in triplicate and good cobalt recoveries (100 ± 1.5%) obtained. Light exposure was minimized to prevent photochemical degredation of $[(NH_3)_5Co(SCN)]^{2+}$ (especially of the S-bonded isomer), and strongly acid (pH <1) conditions were avoided to prevent the curious HNCS-catalyzed rearrangement[17] of $[(NH_3)_5CoSCN]^{2+}$ to $[(NH_3)_5CoNCS]^{2+}$.

Blank experiments under identical conditions but using $[(NH_3)_5CoOH_2]^{3+}$ in place of the $CF_3SO_3^-$ or FCH_2CONH_2 complexes were carried out to determine the corrections for the subsequent SCN^- anation reaction.[11] These were small but not negligible. Typically, samples of $[(NH_3)_5CoOH_2](ClO_4)_3$ (1.0 g) dissolved in the $SCN^-/SO_4^{2-}/HSO_4^-$ mixture (ca. 40 mL; 25.0 °C) were allowed to react in the dark at 25.0 °C for 6.0 h. After the reactions were quenched by dilution (600 mL H_2O), the mixture was chromatographed on Dowex and, in separate experiments, on Sephadex as described above to determine the components. At least duplicate experiments were carried out.

The prospect that $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ was competitively hydrolyzed by C–N cleavage (observed for some amide-*O* species in basic solution),[13,19] or led to some amide-*O* to amide-*N* rearrangement (observed for analogous urea-*O* species above pH ~4[20]), was checked in separate experiments by hydrolyzing sizeable samples of the complex (~1.0 g) in H_2O (pH 1–4) and chromatographing the products on Sephadex (0.3 M NaCl eluent, pH 7 (phosphate)). Only $[(NH_3)_5CoOH_2]^{3+}$ was observed; any coformed $[(NH_3)_5CoO_2CCH_2F]^{2+}$ or $[(NH_3)_5CoNHCOCH_2F]^{2+}$ elutes in front of the aqua complex under the conditions.[21] It is concluded that <0.5% reaction occurs via these routes.

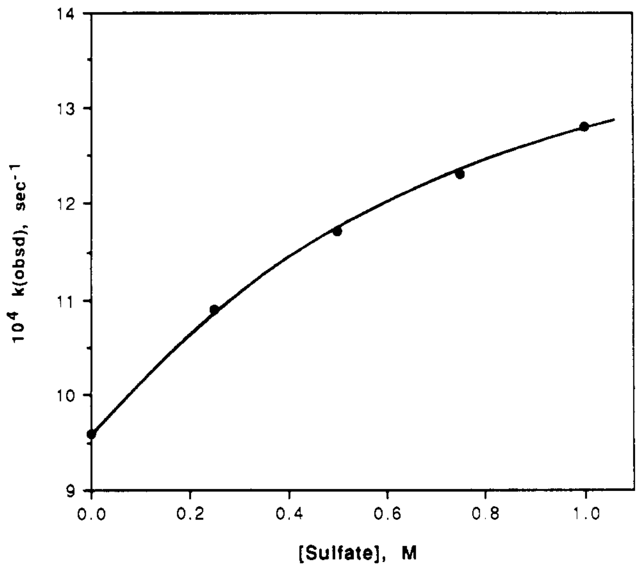

Figure 1. Observed specific rate of acid hydrolysis for $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ as a function of $[SO_4^{2-}]$, I = 3.1 M (NaSCN) at 25 °C.

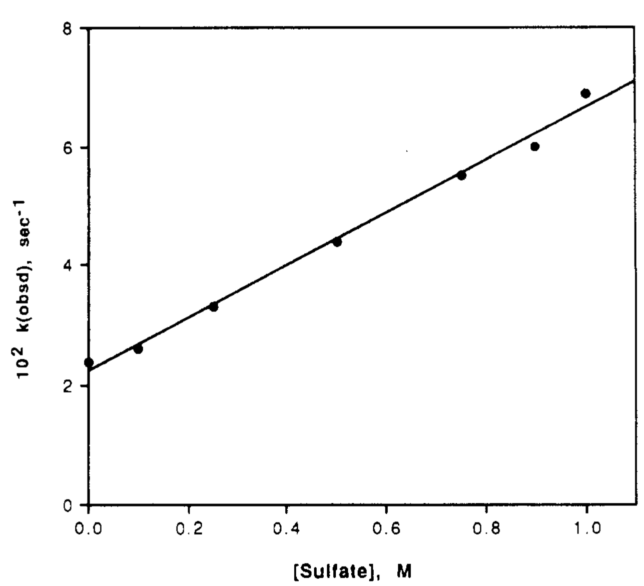

Figure 2. Observed specific rate of acid hydrolysis for $[(NH_3)_5CoO_3SCF_3]^{2+}$ as a function of $[SO_4^{2-}]$, I = 3.1 M (NaSCN) at 25 °C.

Results

Kinetics. The rates of hydrolysis of $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ and $[(NH_3)_5CoO_3SCF_3]^{2+}$ were determined as a function of $[SO_4^{2-}]$ in the range 0–1.0 M, at 25 °C. Mixtures of NaSCN (3.1 M) and Na_2SO_4 (1.0 M) containing $NaHSO_4$ (0.1 M) were used to maintain the ionic strength at 3.1 M.[21] $NaHSO_4$ was employed to "buffer" the SO_4^{2-} and to keep the pH sufficiently low (ca. 3) to prevent any contribution to the rate from the base-catalyzed[13,21,22] pathway. For the same reason, runs in neat SCN^- solution were conducted at pH ca. 3 ($HClO_4$).

The rate data (Tables I and II (supplementary material)) are shown plotted (Figures 1 and 2) to illustrate the effect of SO_4^{2-}. For the 3+ $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ complex, the form of the k(obsd) vs $[SO_4^{2-}]$ curve is indicative of significant ion-pair formation at higher $[SO_4^{2-}]$. The definite although not marked flattening as $[SO_4^{2-}]$ approaches 1 M indicates the approach of

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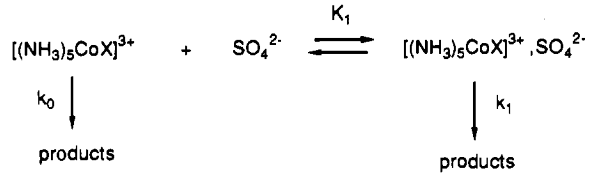
ion-pair saturation, and this would be anticipated[7] for a 3+,2− interaction at $I = 3$ M. The rate data were analyzed according to the scheme



for which the following expression is readily derived:

$$k(\text{obsd}) = (k_0 + k_1K_1[SO_4^{2-}])/(1 + K_1[SO_4^{2-}])$$

Weighted nonlinear regression with $k_0 = 9.6 \times 10^{-4}$ s^{-1}, using k_1 and K_1 as parameters, gave $k_1 = (1.6 \pm 0.1) \times 10^{-3}$ s^{-1} and $K_1 = 1.0 \pm 0.4$ M^{-1}. The relatively large uncertainties for k_1 and especially K_1 arise because the curvature is not sharp and, also, since k_1 is not much greater than k_0, the error (±5%) in k(obsd) contributes. This does not materially affect the conclusions to be drawn, and we did not attempt to collect more data in the critical lower sulfate region in order to improve the analysis. The value of K_1 may be compared with that determined (1.8) for another 3+ ion, $[Co(NH_3)_6]^{3+}$, in association with SO_4^{2-} at the same ionic strength of 3 M.[7] Indeed, using $K_1 = 1.8$ rather than 1.0 to fit the present set of data gives a result that is not very different ($10^3k = 1.47 \pm 0.1$ instead of 1.6; Table I (supplementary material)).

The main result is clear—the rate of reaction is increased by the addition of SO_4^{2-} ($k_1/k_0 = 1.53$), in a manner consistent with a 3+,2− ion-pair preequilibrium. Note that the rate data per se do not (nor cannot) indicate much more than this—the elucidation of the mechanism rests with the relationship between the rates and the sulfate dependence of the product distribution.

The triflato complex also shows a rate increase as SCN^- is replaced by SO_4^{2-} at constant ionic strength (Figure 2). It can be seen that (i) the rate increase for anionic $CF_3SO_3^-$ as a leaving group is more marked than that for neutral FCH_2CONH_2 and (ii) limiting rate behavior is not observed. Indeed the plot of k(obsd) vs $[SO_4^{2-}]$ is essentially linear. However ion pairing between a 2+ cation and SO_4^{2-} at $I = 3$ M is known to be weak, although measurable (K_{IP} for $[(NH_3)_5CoNCS]^{2+},SO_4^{2-}$, a reasonable analogue, is 0.5[7]). Presumably the slight hyperbolic curvature is hidden in the experimental error (k, ±5%); there is probably also some compensating factor such as variation in activity coefficients as SCN^- is replaced by SO_4^{2-}, despite the nominally constant ionic strength.[23-25]

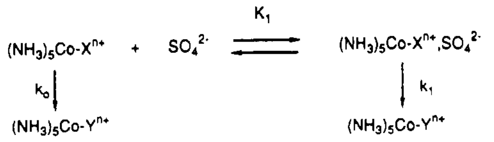
We can nonetheless analyze the data according to the relation $k(\text{obsd}) = (k_0 + k_1K_1[SO_4^{2-}])/(1 + K_1[SO_4^{2-}])$ and use $K_1 = 0.5$, which is the value determined for the related system $[(NH_3)_5CoNCS]^{2+},SO_4^{2-}$ under similar conditions. The results ($k_0 = (2.4 \pm 0.1) \times 10^{-2}$; $k_1 = (14 \pm 2) \times 10^{-2}$ s^{-1}) come from a reasonable data fit (Table II (supplementary material)) and indicate that the ion pair is ca. 6 times more reactive than the free ion.

The analyses above have ignored the prospect of ion pairing by SCN^-. If this possibility is included in a revised ion-pair reaction scheme (but excluding ion-triplet formation), a rate law of identical form is obtained

$$k(\text{obsd}) = (k^*_0 + k^*_1K^*_1[SO_4^{2-}])/(1 + K^*_1[SO_4^{2-}])$$

but where the constants k^*_0, k^*_1, and K^*_1 now have the significance $k^*_0 = (k_0 + 3.1k_2K_2)/(1 + 3.1K_2)$, $k^*_1 = (k_1K_1 - 3.1k_2K_2)/(K_1 + 3.1K_2)$, and $K^*_1 = (K_1 - 3.1K_2)/(1 + 3.1K_2)$, where k_2 and K_2 are the corresponding specific rate and ion-pair constants for $[(NH_3)_5CoL]^{n+},SCN^-$. One effect of ion pairing by SCN^- is a reduction in the apparent ion-pair constant for SO_4^{2-} (K^*_1). However, this apparent constant K^*_1, or ion-pair constant relative to SCN^-, is probably not very different from the ion-pair constant measured[2] relative to ClO_4^-,[7] if SCN^- and ClO_4^- ion pair to similar extents (as seems likely[24,25]). Furthermore, the apparent reactivity of the SO_4^{2-} ion pair, k^*_1, will be a little larger than the true value k_1, while the apparent value for the reactivity of the free ion, k^*_0, will be slightly reduced or increased depending upon whether k_2 is smaller or greater than k_0 (and it appears to be smaller[26]). For the present purposes, these subtleties are not of major concern while SO_4^{2-} dominates the ion pairing.

Table III. Hydrolysis of $[(NH_3)_5CoX]^{n+}$ in SO_4^{2-}/SCN^- ($I = 3.1$ M, 25 °C)



[Y = SCN^-, NCS^-, OH_2 and OSO_3^{2-}]

	% population[a]		% reaction[b,c]	
$[SO_4^{2-}]$, M	% free ion	% ion pair	% via free ion	% via ion pair
X = $CF_3SO_3^-$ ($10^3k_o = 2.4$, $10^3k_1 = 14$, $K_1 = 0.5$)				
0	100	0	100	0
0.1	95.2	4.8	77.4	22.6
0.25	88.9	11.1	57.8	42.2
0.5	80.0	20.0	40.7	59.3
0.75	72.7	27.3	37.4	68.6
1.0	66.7	33.3	25.5	74.5
X = FCH_2CONH_2 ($10^4k_o = 9.6$, $10^4k_1 = 16$, $K_1 = 1.8$)				
0	100	0	100	0
0.25	69.0	31.0	57.1	42.9
0.5	52.6	47.4	40.0	60.0
0.75	42.6	57.4	30.8	69.2
1.0	35.7	64.3	25.0	75.0

[a] % free ion = $10^2/(1 + K_1[SO_4^{2-}])$; % SO_4^{2-} ion pair = $10^2K_1[SO_4^{2-}]/(1 + K_1[SO_4^{2-}])$ = 100 − (% free ion). [b] % reaction via free ion = $10^2k_o/k(\text{obsd})(1 + K_1[SO_4^{2-}]) = 10^2k_o/(k_o + k_1K_1[SO_4^{2-}])$; % reaction via SO_4^{2-} ion pair = $10^2k_1K_1[SO_4^{2-}]/k(\text{obsd})(1 + K_1[SO_4^{2-}]) = 10^2k_1K_1[SO_4^{2-}]/[k_o + k_1K_1[SO_4^{2-}])$ = 100 − (% reaction via free ion). [c] The overall uncertainty in the % populations rests with the accuracy of K_1, while for the % reaction via the SO_4^{2-} ion pair (and free ion) it rests mainly with the accuracies of both k_1 and K_1 (refer to text).

A reviewer has suggested that the ion-triplet $[(NH_3)_5CoX]^{n+},SCN^-,SO_4^{2-}$ could be important in the SCN^- entry pathway, especially if SO_4^{2-} and SCN^- were on opposite sides of the complex and SCN^- were adjacent to the leaving group X. This amounts to having an enhanced reactivity toward SCN^- entry to compensate for its relatively lower abundance. This suggestion while reasonable in itself gets no support from the facts (vide supra). The product distributions, as measured by $[(NH_3)_5CoSCN]^{2+}/[(NH_3)_5CoNCS]^{2+}$ and R_{SCN^-}, are independent of $[SO_4^{2-}]$ for both reactants.

The free-ion/ion-pair populations and more importantly the proportions of the reaction proceeding via the free ion (FI) and sulfate ion pair (IP) at any given $[SO_4^{2-}]$ (0–1 M) are readily calculated with the simple model of a free ion and sulfate ion pair. The results (Table III) reveal that for both the $[(NH_3)_5CoO_3SCF_3]^{2+}$ and $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ hydrolysis reactions, more than 50% of the reaction proceeds via the SO_4^{2-} ion pair above ca. 0.3 M sulfate ion, and up to 75% at the 1 M level. The near coincidence in these numbers for the two systems arises from the fortuitous circumstance that the lower abundance of the triflato ion pair is almost precisely compensated by its greater reactivity.

The effect of ion pairing on hydrolysis rates of complexes of Co(III), Cr(III), and other metal ions is well-known.[27] Sulfate

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[23] Note that total $[Na^+]$ is not constant for mixtures of the 1:1 and 2:1 electrolytes at the same ionic strength; some prefer to keep $[Na^+]$ constant rather than the formal ionic strength.

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Table IV. Product Distributions for the Spontaneous Hydrolysis[a] of $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ in SO_4^{2-}/SCN^- (I = 3.1 M, 25.0 °C)

$[SO_4^{2-}]$, M[b]	$[SCN^-]$, M	% $CoOSO_3^+$[i,j]	$10^2R_{SO_4^{2-}}$[c]	% $\sum[Co(SCN)^{2+}]$[d]	S/N[e]	% S-bonded[f]	$10^2R_{SCN^-}$[g]
0	3.1	0		15.4 (3)	0.94	48.5	5.9
0.25	2.325	1.6 (1)	6.8	12.4 (2)	0.95	48.5	6.2
0.50	1.55	3.2 (1)	6.6	8.9 (2)	0.88	47	6.5
		3.2 (2)[h]	6.6	8.7 (3)[h]	0.86	46	6.4
0.75	0.775	4.6 (1)	6.2	4.8 (4)	0.83	45.5	6.8
1.0	0	7.1 (2)	6.8	0			
av			6.6 ± 0.3		0.88 ± 0.05	47 ± 1.5	6.4 ± 0.4

[a] Reaction time 90 min, except for footnote *h*. [b] $[Na_2SO_4]:[NaHSO_4]$ = 10:1; only $[SO_4^{2-}]$ is tabulated. [c] $R_{SO_4^{2-}} = [CoOSO_3^+]/[CoOH_2^{3+}]([SO_4^{2-}] + [HSO_4^-])$. [d] % ($CoSCN^{2+}$ plus $CoNCS^{2+}$); corrected for $Co(SCN)^{2+}$ arising from subsequent anation of $CoOH_2^{3+}$ by SCN^- (see text). [e] $CoSCN^{2+}/CoNCS^{2+}$. [f] 10^2 % $CoSCN^{2+}$/% ($CoSCN^{2+}$ + $CoNCS^{2+}$) = $10^2(S/N)/(1 + (S/N))$. [g] $R_{SCN^-} = [Co(SCN)^{2+}]/[CoOH_2^{3+}][SCN^-]$. [h] Reaction time 150 min. [i] Corrected for $CoOSO_3^+$ arising from subsequent anation of $CoOH_2^{3+}$ by SO_4^{2-} (refer to text). [j] The number of determinations is given in parentheses; the sulfato complex was determined separately from $Co(SCN)^{2+}$ by using Dowex resin; all other determinations employed Sephadex resin.

Table V. Product Distributions for the Reaction of $[(NH_3)_5CoO_3SCF_3]^{2+}$ in SO_4^{2-}/SCN^- Media (I = 3.1 M, 25 °C)

$[SO_4^{2-}]$, M[a]	% $CoOSO_3^+$	$10^2R_{SO_4^{2-}}$[b]	% $\sum[Co(SCN^{2+})]$[c]	$10^2R_{NCS^-}$[d]	% S-bonded	S/N[e]
0	0		13.3	4.9_5	55.5	1.25
0.25	*f*		10.4	4.9_9	55.5	1.24
0.50	*f*		6.85	4.7_4	56.5	1.31
0.75	*f*		3.65	4.8_9	54.5	1.20
1.00	2.9 (3)	3.0	0			
av[g]		3.0[h]		$4.8_9 \pm 0.1_1$	55.5 ± 1.0	1.25 ± 0.05

[a] $Na_2SO_4/NaHSO_4$ (10:1) and NaNCS used to maintain ionic strength; stoichiometric $[Na_2SO_4]$ is listed; [NaSCN] = 3.1 (1 − $[Na_2SO_4]$). [b] $R_{SO_4^{2-}}$ = (% $CoOSO_3^+$)/(% $CoOH_2^{3+}$)$[SO_4^{2-}]$. [c] % ($CoSCN^{2+}$ + $CoNCS^{2+}$). [d] R_{SCN^-} = (% [$CoSCN^{2+}$ + $CoNCS^{2+}$])/(% $CoOH_2^{3+}$)$[SCN^-]$. [e] (% $CoSCN^{2+}$)/(% $CoNCS^{2+}$). [f] Not measured; ∑Co normalized to 100% on the basis of observed products. [g] Mean and standard deviations quoted. [h] Triplicate result for single $[SO_4^{2-}]$.

ion features prominently among a range of Y^{m-} anions examined, and as we find also, the result is usually an acceleration. This has been widely interpreted as evidence for dissociative activation of the hydrolysis reaction on the grounds that charge separation of an anionic leaving group from a positively charged metal ion is facilitated by charge neutralization through ion pairing. This view receives some support from our results, since the reaction of the triflato species, which involves an anionic leaving group, is considerably more accelerated than for the fluoroacetamide complex, which has a neutral leaving group. Note however that even for the dissociation of a neutral leaving group the effects of ion pairing can be significant (50% rate increase). This point is relevant to the anation reactions of aqua metal ions in general,[28] where commonly it is assumed (wrongly) that water exchange in the ion pair is the same as that in the free ion.

Production Distributions. In SO_4^{2-} solution, a small although readily detectable amount of $[(NH_3)_5CoOSO_3]^+$ is produced, along with the major product $[(NH_3)_5CoOH_2]^{3+}$. In the SO_4^{2-}/SCN^- mixtures, N- and S-bonded $[(NH_3)_5Co(SCN)]^{2+}$ are produced as well and easily separated from the 1+ and 3+ ions by ion-exchange chromatography. The determination of the total and individual $[(NH_3)_5Co(SCN)]^{2+}$ ions has been described in detail elsewhere.[8,10,11] The dependence upon $[SO_4^{2-}]$ of the $[(NH_3)_5CoSCN]^{2+}/[(NH_3)_5CoNCS]^{2+}$ ratios, and the total $[(NH_3)_5CoSCN]^{2+}$ + $[(NH_3)_5CoNCS]^{2+}$ products formed are presented in Tables IV and V (Figures 3 and 4) for the reactions of the $[(NH_3)_5CoOC(NH_2)CH_2F)]^{3+}$ and $[(NH_3)_5CoO_3SCF_3]^{2+}$ complexes, respectively.

The important features of these results are (i) the linear dependences of the $[(NH_3)_5Co(SCN)]^{2+}/[(NH_3)_5CoOH_2]^{3+}$ ratios on $[SCN^-]$ (or $[SO_4^{2-}]$, noting that $[SCN^-] + 3.1[SO_4^{2-}]$ = constant = 3.1 M) for each of the $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ (Figure 3) and $[(NH_3)_5CoO_3SCF_3]^{2+}$ (Figure 4) reactions and (ii) the constancy of the $[(NH_3)_5CoSCN]^{2+}/[(NH_3)_5CoNCS]^{2+}$ ratios, independent of $[SCN^-]$, but clearly dependent upon the leaving group, $CF_3SO_3^-$ or FCH_2CONH_2. We note that the total SCN^- competition is somewhat higher (~20%) for the more strongly ion-pairing 3+ substrate, $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$,

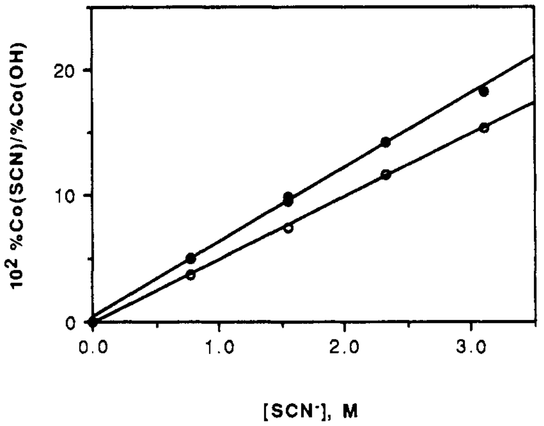

Figure 3. Product ratio % Co(SCN)/% $CoOH_2$ as a function of $[SCN^-]$ in SCN^-/SO_4^{2-} mixtures for I = 3.1 M at 25 °C.

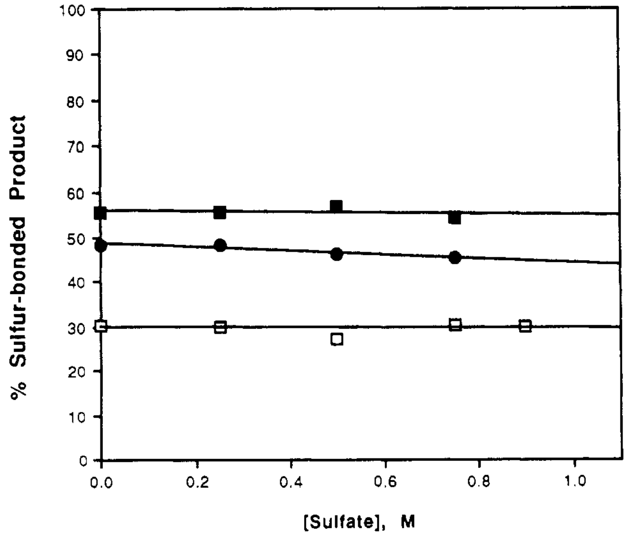

Figure 4. % CoSCN of total CoSCN + CoNCS product for the SCN^- substitution reactions of $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ (●), $[(NH_3)_5CoO_3SCF_3]^{2+}$ (■), and $[(NH_3)_5CoOH_2]^{3+}$ (□) as a function of $[SO_4^{2-}]$, illustrating the role of the leaving group and lack of effect of $[SO_4^{2-}]$ (I = 3.1 M (NaSCN), 25 °C).

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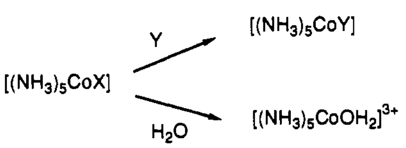
Table VI. Product Distributions for the Controlled Anation (6.0 h) of $[(NH_3)_5CoOH_2]^{3+}$ in SO_4^{2-}/SCN^- Media (I = 3.1 M, 25 °C)

$[SO_4^{2-}]$, M[a]	$[SCN^-]$, M	% $CoOSO_3^+$ [b,c]	% $\sum Co(SCN)^{2+}$ [c,d]	S/N[e]	% S-bonded	Q[f]
0	3.1	0	4.91 (4)	0.441	30.5	*g*
0.25	2.325	2.04 (2)	3.01 (4)	0.427	30.0	0.15_9
0.5	1.55	3.33 (4)	1.54 (4)	0.374	27.0	0.14_9
0.75	0.775	4.57 (2)	0.677 (4)	0.439	30.5	0.14_3
0.9	0.31		0.232 (2)	0.406	29	*g*
1.0	0	5.54 (2)				
av				0.417 ± 0.025	29.4 ± 1.3	0.15 ± 0.01

[a] $[SO_4^{2-}]$ only; total sulfate = $[SO_4^{2-}] + [HSO_4^-]$; $[SO_4^{2-}]:[HSO_4^-]$ = 10:1. [b] The number of determinations is given in parentheses. [c] The sulfato complex was determined separately from $Co(SCN)^{2+}$ by using Dowex resin; all other determinations employed Sephadex resin. [d] $CoSCN^{2+} + CoNCS^{2+}$. [e] $CoSCN^{2+}/CoNCS^{2+}$. [f] $Q = [Co(SCN)^{2+}][SO_4^{2-}]/([CoOSO_3^+][SCN^-])$. [g] Indeterminate.

although as noted previously,[7,8] such an observation is not meant to imply a specific product-determining role for the ion-paired substrate.

Early kinetic studies of the role of ion pairs in aquation reactions invariably assumed that the ion-pairing agent was noncoordinating; i.e., it is not incorporated *during* the hydrolysis process.[27] Yet careful ion-exchange studies of the reaction products for the so-called spontaneous aquation reactions[8,29–32] can reveal significant anion competition, and this observation coupled with kinetic studies can be used to advantage to probe mechanism. The present work shows that SCN^- and even SO_4^{2-} can compete, and this is yet another study showing that direct anion insertion can occur during the accompanying spontaneous hydrolysis reaction



albeit the competition is usually small; e.g., X = $CF_3SO_3^-$, Y = Cl^- (1 M), 3% $[(NH_3)_5CoCl]^{2+}$). We have shown that reactant ions such as $[(NH_3)_5CoONO_2]^{2+}$ and $[(NH_3)_5CoOP(OCH_3)_3]^{3+}$ of even moderate lability can be handled provided the necessary (although small) corrections for the subsequent anation reaction are made.[8,26,33]

Sulfate and Thiocyanate Ion Anation of the Aqua Complex. In this work parallel studies of the (slow) anation reaction of the $[(NH_3)_5CoOH_2]^{3+}$ ion in identical SCN^-/SO_4^{2-} media were carried out to determine the corrections for the anion competition observed for the fluoroacetamide complex hydrolysis (6 h, 25 °C). These data are given in Table VI. For water exchange at 25 °C the $t_{1/2}$ is ca. 30 h in the absence of added anions,[34,35] and the rate is reported to be the same at very high sulfate concentration.[35] There are no data for the "middle" region ($[SO_4^{2-}]$ ca. 1 M), and it is conceivable that here the rate of water exchange is different. This cannot be gauged from our measurements. We have determined the extent of incorporation of both SO_4^{2-} and SCN^-, as a function of $[SO_4^{2-}]$, for a fixed (6 h) reaction time, and only the *relative* extents of SCN^- and SO_4^{2-} anion competition are conceivably of intrinsic mechanistic significance, save for the observation of any effect of SO_4^{2-} on the S- to N-bonded SCN^- product ratio.

The results show that SO_4^{2-} has no measurable effect on the S- to N-bonded $[(NH_3)_5Co(SCN)]^{2+}$ product ratio accompanying the water-exchange process, consistent with the observations reported here for the two other leaving groups, $CF_3SO_3^-$ and FCH_2CONH_2. This result is also consistent with our observations on the induced aquation[8] and base hydrolysis[10] reactions for different counteranions including SO_4^{2-}. The S/N ratio is however leaving-group dependent for reactions in acid solution and especially for the so-called spontaneous hydrolysis reactions[8] (the "slow" reactions).

Although we have not monitored water exchange for the ion pairs, we can use the conventional[12] competition ratios R_{SCN^-} and $R_{SO_4^{2-}}$ by taking their ratio so that it does not involve the aqua product:

$$R_{SCN^-} = [As_5Co(SCN)^{2+}]/[AsCoOH_2^{3+}][SCN^-]$$

$$R_{SO_4^{2-}} = [A_5CoOSO_3^+]/[AsCoOH_2^{3+}][SO_4^{2-}]$$

Thus

$$R_{SCN^-}/R_{SO_4^{2-}} = [A_5Co(SCN)^{2+}][SO_4^{2-}]/[A_5CoOSO_3^+][SCN^-]$$

The values of this quotient (=Q) for three different concentrations of SCN^- where both SO_4^{2-} and SCN^- incorporation were determined are shown in Table VI; Q is constant. Interestingly, this observation is not mechanistically diagonstic—it can be shown that this ratio *should* be constant, whether anation proceeds directly via ion pairs or via a reduced coordination intermediate—and so the constancy merely provides an internal check on the competition numbers; as shown below, it is the parallel water entry path that provides the mechanistic discrimination.

Predictions Based on the Interchange (Ion-Pair) Mechanism. The anion competition coupled with the kinetic data can be used to calculate the efficiency of collapse of the ion pairs, i.e., anion vs solvent incorporation. We examine first the conventional model[28] of a preassociation mechanism where Y entry arises from only $[A_5CoL]^{n+},Y^{m-}$ preformed ion pairs, while, according to this model, H_2O entry can arise from $[A_5CoL]^{n+}$ as well as $[A_5CoL]^{n+},Y^{m-}$, since both contain H_2O in the immediate solvation sheath because of perpetual encounter with the bulk solvent.

No assumption need be made about the mode of activation—dissociative or associative—only that it is an interchange process with no reduced or increased coordination number intermediate. At 1.0 M SO_4^{2-}, the $[(NH_3)_5OC(NH_2)CH_2F]^{3+}$ hydrolyses 25% by way of the free ion (Table III), which gives only $[(NH_3)_5CoOH_2]^{3+}$, and 75% by way of $[(NH_3)_5OC(NH_2)CH_2F]^{3+},SO_4^{2-}$ from which, according to this model, any $[(NH_3)_5CoOSO_3]^+$ (x%) must arise, together with $[(NH_3)_5CoOH_2]^{3+}$ (100 − x%). From the observed 6.8% sulfato complex (Table IV) a value for x is calculated, $-6.8 = 0.25(0) + 0.75(x)$, indicating inefficient (9.1%) collapse for the ion pair. A similar calculation for the $[(NH_3)_5CoO_3SCF_3]^{2+}$ reaction, using the data of Tables III and V, leads to an efficiency of collapse of 4.0%.

Similar calculations cannot be made as precisely for the reactions in 3.1 M SCN^-, since the relevant ion-pair constants are unknown. However, we shall see that this is inconsequential to the main conclusions derived from the results for SCN^-/SO_4^{2-} media, provided we can be sure that the SO_4^{2-} ion pairs are sufficiently more abundant and/or more reactive than SCN^- ion pairs, such that a significant proportion of the reaction is via $[(NH_3)_5CoL]^{n+},SO_4^{2-}$ in the "middle" SCN^-/SO_4^{2-} region [$[SCN^-]$ = 3.1/4 to 3.1 × 3/4 M; i.e., $[SO_4^{2-}]$ = 0.775–2.325 M).

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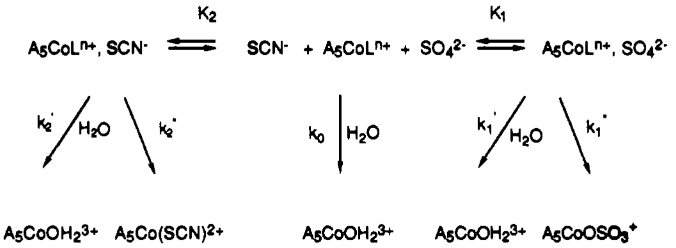
As regards significant abundance of $[(NH_3)_5CoL]^{n+}$, SO_4^{2-}, this is certainly the case (Table III). There seems little doubt that a 2- anion more effectively ion pairs than a 1- anion, and we will assume, conservatively, that SCN^- ion pairs more weakly than SO_4^{2-} by a factor of 5, for both the 2+ and 3+ reactants. K_1 values (0.36, 0.1) so assumed are consistent with known trends[7] in K_1 values as the formal charges of the component ions are changed. We also assume the free ion and SCN^- ion pairs are of comparable reactivity and for simplicity set $k_0 = k_1$.

In order to deal persuasively with the mixed SCN^-/SO_4^{2-} competition data, we need some idea, albeit imprecise, of the efficiency of SCN^- capture from its ion-pair $[(NH_3)_5CoL]^{n+}$, SCN^-. These efficiencies, calculated on the basis of the assumptions above, are 31% for $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$, SCN^- and 56% for collapse of $[(NH_3)_5CoO_3SCF_3]^{2+}$,$SCN^-$. As for SO_4^{2-}, the anion capture from the ion pair appears to depend upon the leaving group, and SCN^- is a more effective competitor than SO_4^{2-}, for both the $CF_3SO_3^-$ and FCH_2CONH_2 leaving groups, according to this model. Obviously the calculated capture efficiencies for SCN^- will change as the values of K_1 (of uncertain magnitude) are varied, but any ***reasonable*** values lead to the same conclusion. We emphasize that all these analyses are based upon the preassociation or ion-pair mechanistic model.

Mixed-Anion Competition. The competition results (Tables IV and V; Figures 3 and 4) for the separate SCN^- and SO_4^{2-} media can now be coupled with the rate data (Tables I and II (supplementary material); Figures 1 and 2) to make specific predictions about the $[SO_4^{2-}]$ dependence of the SCN^- competition, and herein lies the key result of this work. Qualitatively, an increase in $[SO_4^{2-}]$ drives most of the reaction via the SO_4^{2-} ion pair, which, according to our analysis for an interchange (ion-pair) mechanism, gives a little $[(NH_3)_5CoOSO_3]^+$ but mostly $[(NH_3)_5CoOH_2]^{3+}$ and, if the prospect of an ion triplet is ignored, no $[(NH_3)_5Co(SCN)]^{2+}$ product. Thus, SO_4^{2-} should significantly reduce SCN^- capture, over and above the normal (linear) reduction expected, because bulk SO_4^{2-} is replacing bulk SCN^- ($3.1[SO_4^{2-}] + [SCN^-] = 3.1$ M, the constant ionic strength condition).[36] Quantitatively, the proportion of products that is $[(NH_3)_5Co(SCN)]^{2+}$ [37] can be derived for this interchange scheme



We use the conventional R factor[12] (e.g. $R_{SCN^-} = [(NH_3)_5Co(SCN^{2+})]/[(NH_3)_5CoOH_2^{3+}][SCN^-]$) to define the product distribution, since this description removes the normal variation of % competition product with varying $[SCN^-]$ and permits focus on the $[SO_4^{2-}]$ dependence of R. The above scheme leads to the relationship:

$$R_{SCN^-} = [A_5Co(SCN)^{2+}]/[A_5CoOH_2^{3+}][SCN^-] = \frac{k_2''K_2}{k_0 + k_2'K_2[SCN^-] + k_1'K_1[SO_4^{2-}]}$$

Using the data of Tables III–V and the condition $3.1[SO_4^{2-}] + [SCN^-] = 3.1$ leads to

$$R_{SCN^-} = \frac{0.0303}{1 - 0.170[SCN^-]} = \frac{0.0640}{1 + 1.11[SO_4^{2-}]}$$

for the reactions of the $[A_5CoOC(NH_2)CH_2F]^{3+}$ ion, and for the reactions of the $[A_5CoO_3SCF_3]^{2+}$ ion

$$R_{SCN^-} = \frac{0.0146}{1 - 0.226[SCN^-]} = \frac{0.0488}{1 + 2.26[SO_4^{2-}]}$$

A reduction in R_{SCN^-} with increasing $[SO_4^{2-}]$ is predicted for the reaction of both complexes by this mechanism. Figures 5 and 6 vividly illustrate this predicted behavior, in comparison with that observed. The deviations from the observed behavior are large, especially for the reactions of the triflato species, and outside experimental error for the values used to compute the curves.

The constancy of the R values indicates that ion pairs do not lead directly to anation products as the preassociation (or ion-pair) model assumes, although it is clear that ion pairs are formed and substantially affect the substitution rates.

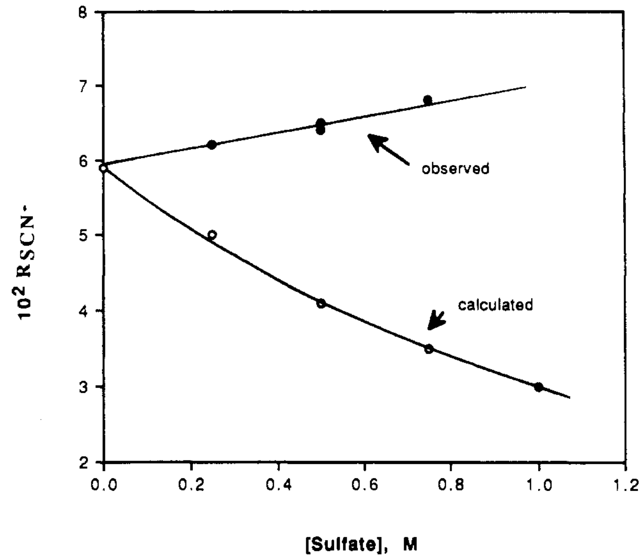


Figure 5. Observed SCN^- competition ratio vs that predicted for the ion-pair (or preassociation) mechanism for SCN^- competition accompanying the acid hydrolysis of the $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$ ion in SCN^-/SO_4^{2-} mixtures for $I = 3.1$ M at 25 °C.

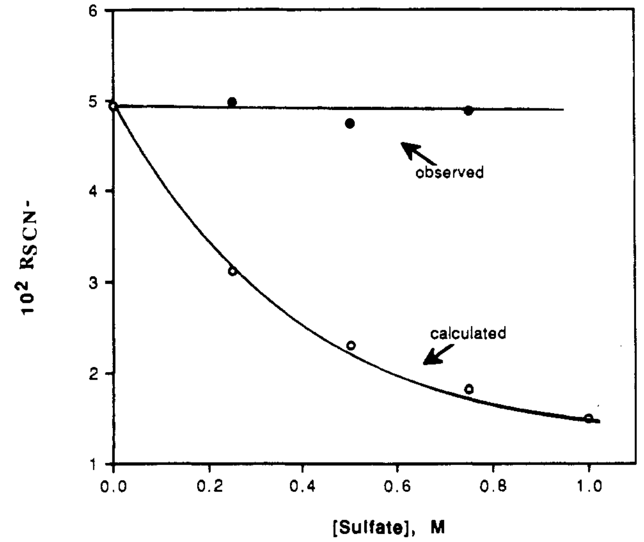


Figure 6. Observed SCN^- competition ratio vs that predicted for the ion-pair or preassociation mechanism for SCN^- competition accompanying the acid hydrolysis of the $[(NH_3)_5CoO_3SCF_3]^{2+}$ ion in SCN^-/SO_4^{2-} mixtures for $I = 3.1$ M at 25 °C.

Discussion

Several recent papers have dealt with anion competition accompanying hydrolysis for the substitution reactions of $[(NH_3)_5CoX]^{n+}$ complexes.[3,4,8,29-32] In general, the product distributions are dependent upon the leaving group, and the extent of anion competition appeared to correlate with the reactivity of

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[36] It is implicitly assumed that the A_5CoL,SO_4 and A_5CoL,SCN ion pairs behave in mixed SCN^-/SO_4^{2-} media as they do in separate SO_4^{2-} or SCN^- media.

[37] The entry of SCN^- leads to both N- and S-bonded SCN^- products, but their parallel production (invariant with $[SCN^-]$) allows the simplification of using single-constant descriptions.

Inorg. Chem. **1990**, *29*, 4683-4687 **4683**

the complex.[8] Except for the base-hydrolysis reaction,[10] the S- to N-bonded product ratio was also leaving-group dependent, even within the induced aquation group of reactions, and there was no obvious correlation of this S- to N-bonded ratio, or the total SCN^- competition, with ion pairing of the reactants.[8] These results appear to preclude a classic pentacoordinate intermediate $[(NH_3)_5Co]^{3+}$, but they also seem to eliminate ion pairs as the direct source of competition products.

Mixed-anion studies were initiated to probe this aspect further.[3,4] In particular, the effect of the more strongly ion-pairing anion SO_4^{2-} for a range of different competitors was examined for the classic induced aquation, nitrosation of $[(NH_3)_5CoN_3]^{2+}$, a reaction for many years believed to involve the reduced coordination number intermediate $[(NH_3)_5Co]^{3+}$. The results of this work showed that, while anions certainly affected the rate, SO_4^{2-} had no effect on the competition. The widely accepted preassociation mechanism was therefore in trouble on this important aspect.

The present work was undertaken in the belief that the effects of ion pairing both on rate and products could be quantified much more readily for the simple spontaneous aquation reactions because the rate law should not suffer the complications found[3,4] for induced aquation. This has proven to be so. In the present work we have shown that SCN^- competes with water for the vacated coordination site arising in the substitution process in precisely the same way when $[(NH_3)_5CoX]^{n+}$ is the reactant ion (or the $[(NH_3)_5CoX]^{n+},SCN^-$ ion pair) as when the $[(NH_3)_5CoX]^{n+}, SO_4^{2-}$ ion pair is the reactant.

This remarkable result emphasizes our continued view that preassociation of the competing anion is not required for direct product formation. Rather, there must be a common product-determining species formed from the free cation or any of its ion pairs because anion entry is not rate determining, and this species survives for a time sufficient to sample its inherited ion atmosphere. For the $[(NH_3)_5CoX]^{n+}$ substitution chemistry, we maintain that this intermediate is the very short lived $[(NH_3)_5Co]^{3+}$, despite being a species of demonstrably variable lifetime[8] that appears to depend upon its rate of generation.

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Supplementary Material Available: Tables I and II, listing kinetic data (2 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
The University of Wisconsin—Milwaukee, P.O. Box 413, Milwaukee, Wisconsin 53201

Ligand-Scrambling Reactions of Cyano(trialkyl/triarylphosphine)gold(I) Complexes: Examination of Factors Influencing the Equilibrium Constant

Anne L. Hormann-Arendt and C. Frank Shaw III*

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The ligand-scrambling reaction of R_3PAuCN (to form $(R_3P)_2Au^+$ and $Au(CN)_2^-$) has been studied for R = Ph, Me, Et, *i*-Pr, and Cy (Cy = cyclo-C_6H_{11}).[1] The reactions are conveniently studied by ^{31}P and ^{13}C NMR spectroscopy. The phenyl complex undergoes rapid ligand exchange and must be cooled to approximately 240 K to observe sharp resonances for the individual equilibrium components. All of the aliphatic complexes are in the slow exchange limit allowing observation by NMR spectroscopy at room temperature. The cyclohexyl complex equilibrated slowly, requiring several days to reach equilibrium, while the other complexes equilibrated within the time required to measure the spectrum. Equilibrium constants ($K_{eq} = [(R_3P)_2Au^+][Au(CN)_2^-]/[R_3PAuCN]^2$) were measured by integration of ^{31}P NMR spectra of methanol solutions of the complexes. For the ethyl complex, K_{eq} is dependent on the initial concentration, $[Et_3PAuCN]_0$, and the ionic strength of the medium. The concentration dependence is attributed to the ionic strength effect of the reaction products. The effects of the phosphine substituents on K_{eq} were compared at 240 K in 0.25M NH_4NO_3 methanol solutions. The K_{eq} values (±esd) are as follows: Ph_3PAuCN, 0.112 ± 0.005; Me_3PAuCN, 0.37 ± 0.05; Et_3PAuCN, 0.24 ± 0.02; *i*-Pr_3PAuCN, 0.29 ± 0.03; Cy_3PAuCN, 0.49 ± 0.02. A convenient new procedure for preparing AuCN, the precursor of R_3PAuCN, from Me_2SAuCl was developed. Of the R_3PAuCN complexes studied, *i*-Pr_3PAuCN and Cy_3PAuCN have not been reported in the literature.

Introduction

Recently, we examined the solid-state structure and solution equilibria of cyano(triethylphosphine)gold(I), Et_3PAuCN.[2] In the solid state, the gold is coordinated to a phosphine and cyanide ligand, but in solution, the complex undergoes a novel ligand scrambling reaction:

$$2Et_3PAuCN \rightleftharpoons (Et_3P)_2Au^+ + Au(CN)_2^- \qquad (1)$$

The equilibrium constant for the reaction was shown to be dependent upon the solvent, increasing with the polarity and/or polarizability of the solvent.

Ligand scrambling reactions of gold(I) complexes that are initiated by the presence of excess ligands have been known for some time.[3] The reaction in eq 1, however, does not require the presence of excess ligand. Its importance is just becoming recognized; such reactions may significantly alter the solution chemistry of gold(I) complexes used in the treatment of rhematoid arthritis.[2,4] Ligand scrambling reactions analgous to eq 1 have been reported for a variety of anionic complexes,[4a,5] but to our knowledge, (mpt)AuCN (mpt = 1-methylpyridine-2-thione)[6] and $(NH_2)_2CSAuI$[7] are the only other neutral gold(I) complexes reported to undergo similar ligand exchange. Two extreme cases of the ligand scrambling reaction given in eq 1 are the complexes (tetrahydrothiophene)gold(I) iodide[8] and (pyridine)chlorogold(I),[9] which exist in the solid state as the ionic complexes $[Au(THT)_2^+][AuI_2^-]$ and $[(py)_2Au^+][AuCl_2^-]$, respectively.

Because of the novelty of this ligand-scrambling reaction and its possible biological implications, the effects of several extrinsic and intrinsic influences on the extent of the reaction were systematically examined. The extrinsic influences examined here are the initial concentration of the complexes, $[R_3PAuCN]_0$, and

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(1) List of abbreviations: Ph = phenyl, Me = methyl, Et = ethyl, *i*-Pr = isopropyl, Cy = cyclohexyl, R_3P = trialkyl/triarylphosphine, R_3PO = trialkyl/triarylphosphine oxide.

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