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Equilibrium Dynamics in the Thallium(III)−Cyanide System in Aqueous Solution

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Ligand exchange reactions of thallium(III) cyano complexes, $Tl(CN)_n^{3-n}$, have been systematically studied in aqueous solution containing 4 M ionic medium $\{[ClO_4^-]_{tot} = 4$ M, $[Na^+]_{tot} = 1$ M, $[Li^+]_{tot} + [H^+]_{tot} = 3$ M$\}$, at 25 °C, using ^{205}Tl and ^{13}C NMR one-dimensional inversion transfer techniques. Rate constants for all dominating exchange pathways were determined and compared to the previously studied thallium(III) halide complexes. Also in the case of cyanide ligands the ligand exchange is dominated by the rare type of reactions occurring *via* a direct encounter of two complexes (self-exchange reactions), e.g. $Tl(CN)_3 + Tl(CN)_2^+ \rightleftharpoons Tl(CN)_2^+ + Tl(CN)_3$ (k_{32}, k_{23}) or $Tl(CN)_2^+ + Tl(CN)_4^- \rightleftharpoons 2Tl(CN)_3$ (k_{24}, k_{33}). The determined cyanide exchange rate constants between complexes $Tl(CN)_m^{3-m}$ and $Tl(CN)_n^{3-n}$, k_{mn}^{rds}, for the rate-determining step have all similar values, about 100−1000 s^{-1}, that are 5 orders of magnitude smaller than for the corresponding halide exchange processes. This indicates the presence of a common rate-determining step for the self-exchange reactions of the cyanide ligand, proposed to be the breaking of the thermodynamically very stable Tl−CN bond. This is in contrast to the Tl(III)−halide systems, where the breaking of the $Tl-OH_2$ bond was proposed to determine the reaction rate. The second type of cyanide exchange, namely anation, has been found only in two cases: $Tl(CN)_2^+ + CN^- \rightleftharpoons Tl(CN)_3$ (k'_{23}, k'_{32}); and $Tl(CN)_3 + CN^- \rightleftharpoons Tl(CN)_4^-$ (k'_{34}, k'_{43}). These reactions are very fast, $k'_{mn} \sim 10^9$ M^{-1} s^{-1}, and are proposed to proceed through an associative interchange mechanism, where the rate-determining step is a water dissociation mediated by the incoming ligand, i.e. similarly as for the corresponding halide complexes. The third type of cyanide exchange reactions was possible to study due to the presence of an NMR-active nucleus (^{13}C) in the ligand. Only the following ligand substitution reaction was observed: $Tl(^*CN)_2^+ + HCN \rightleftharpoons Tl(CN)_2^+ + H^*CN$ ($k^*_{2,\mathrm{HCN}}$, $k^*_{\mathrm{HCN},2}$). The reason for the dominant role of the self-exchange reactions is the very low concentration of free CN^- and the inertness of the HCN species in the ligand exchange reactions. The obtained dynamic information is discussed and compared to the corresponding data for the thallium(III) halide complexes.

Thallium(III) forms very strong complexes with halide ions.[1−6] Recently, the formation of even stronger complexes between Tl(III) and cyanide, $Tl(CN)_n^{3-n}$, $n = 1-4$, was established and their stability constants were determined.[7] The structure of the halide complexes was studied both in solid state and in solution by means of IR,[8] Raman,[9−11] X-ray diffraction,[12,13] and ^{205}Tl NMR spectroscopy.[6] Very recently, a detailed multimethod study was published on the structure, symmetry, and coordination numbers of Tl(III) chloro, bromo, and cyano complexes in aqueous solution.[14] In the first cyano complex Tl(III) is six-coordinated, $TlCN(OH_2)_5^{2+}$. In the second complex, *trans*-$TlCN_2(OH_2)_4^+$, thallium retains the six-coordination; the Tl−CN bond length is almost the same as in the first complex, 2.11 Å, and Tl−O is 2.42 Å, that is 0.2 Å longer than in the hydrated thallium(3+) ion, $Tl(OH_2)_6^{3+}$. Upon formation of the third complex, $Tl(CN)_3(OH_2)$, the coordination number decreases to 4 and the symmetry is C_{3v} with Tl−C 2.15 Å and Tl−O 2.42 Å. The fourth complex is tetrahedral with the Tl−C bond length equal to 2.19 Å.

The dynamics of aluminum group elements has been scarcely studied because of the difficulty to monitor the reactions. The solvent exchange was investigated for aluminum, gallium, and indium.[15−17] The mechanism of the solvent exchange is I_d for Al^{3+} and Ga^{3+}, but it is associative for In^{3+}. The complex formation reactions of Al^{3+} occur by I_d mechanism,[18,19] whereas an associatively activated mechanism was proposed for gallium(III) and is also possible for indium(III).[19] The knowledge about dynamic properties of thallium(III) is even more limited. The kinetics of complex formation with semixylenol orange and 4-(2-pyridylazo)resorcinol were studied by the stopped-flow method.[20,21] The complex $Tl(OH)^{2+}$ was found to be the active

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Table 1. Kinetic Data for Tl(III) Cyano and Halo Complexes

	cyanide		bromide[24]	chloride[23]
	k_{mn}/M^{-1} s^{-1}	k_{mn}^{rds}/s^{-1}	k_{mn}^{rds}/s^{-1}	k_{mn}^{rds}/s^{-1}
k_{01}	<3	<4 × 10^4	4 × 10^8	6 × 10^8
k_{02}	4.1 ± 0.3	9 × 10^2	2 × 10^8	1 × 10^8
k_{12}	<1	<100	6 × 10^6	4 × 10^6
k_{23}	161 ± 9	5.5 × 10^2	3 × 10^7	9 × 10^7
k_{34}	446 ± 14	1.5 × 10^3	8 × 10^7	
k_{24}	712 ± 200	5 × 10^2		
k'_{12}			1 × 10^9	6 × 10^7
k'_{23}	3.4 × 10^9 [a] (7.3 ± 1.4)	1.1 × 10^{10}	6 × 10^{10}	1 × 10^9
k'_{34}	4.5 × 10^8 [a] (16.3 ± 1.5)	1.5 × 10^9	5 × 10^9	2 × 10^9
$k_{\text{HCN},2}$	0.37 ± 0.03	1		

[a] Calculated from the rate constant values of the reverse reactions (in parentheses), using the equilibrium constants from ref 7.

species in complex formation kinetics. Lincoln *et al.* reported a lower limit of the pseudo-first-order rate constant on the Cl^- exchange of the $TlCl_6^{3-}$ complex.[22]

There are only three recent papers dealing in detail with the ligand exchange of hydrated complexed thallium(III) ions in chemical equilibrium.[23−25] In these papers, we established high-field ^{205}Tl NMR spectroscopy as a powerful tool to elucidate exchange paths using the line shape analysis[23,24] and two-dimensional exchange spectroscopy (2D EXSY).[25] Three types of exchange paths were identified for thallium(III) chloride and bromide complexes. The first path is ligand "self-exchange" between complexes with no net chemical change, for example

$$TlBr_2^+ + TlBr_3 \overset{k_{23}}{\rightleftharpoons} TlBr_3 + TlBr_2^+ \tag{1a}$$

The second path is also a ligand exchange between two complexes but involves net chemical change, *e.g.*

$$TlBr^{2+} + TlBr_3 \underset{k_{22}}{\overset{k_{13}}{\rightleftharpoons}} 2TlBr_2^+ \tag{1b}$$

and the third one is the anation or complex formation reaction of thallium(III) complexes, *e.g.*

$$TlBr_2^+ + Br^- \overset{k'_{23}}{\rightleftharpoons} TlBr_3 \tag{2}$$

Rate constants for all dominating ligand exchange pathways were determined for both halide systems (see Table 1). The first type of reaction (eqs 1a,b) is a very rarely encountered kind of ligand exchange related to the inner-sphere electron transfer as far as the ligand-bridged transition state is concerned.[26−29] This exchange pattern dominates at low ligand to metal ratios (*R*), and the reason that it is observable at all is the very low free ligand concentration due to the strong complex formation. Taking into account the effect of different ligands and the activation parameters, a dissociatively activated interchange process was suggested to operate; *i.e.*, after the encounter of two complexes and formation of an outer-sphere complex, leaving of a water ligand from the first coordination sphere of Tl(III) is the rate-determining step.

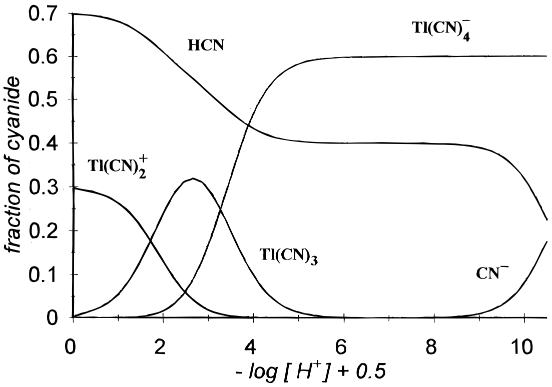

Figure 1. Distribution of cyanide-containing species as a function of the total acid concentration. $[Tl]_{tot}$ = 0.15 M, and $[CN^-]$ = 1.0 M.

The anation reactions, eq 2, dominate the ligand exchange for higher complexes and depend on the entering ligand; therefore, an associatively activated rate-determining step was proposed. This dependence was not very pronounced, and the mechanistic conclusion was somewhat uncertain.[24] Therefore, it was thought that similar data for a more divergent ligand could clarify the situation and a study of the thallium(III) cyano complexes was initiated. The cyanide seemed to be a logical choice because of the following:

(i) It differs significantly from the halides in its bonding character and basicity. (ii) It forms stable complexes with thallium(III), and the equilibria are known.[7] (iii) The structure of the different complexes has been determined.[14] (iv) A recent investigation showed that although no line broadening was observed, the time scales offered by the spin−lattice relaxation times, T_1, in both ^{205}Tl and ^{13}C NMR, are suitable for a dynamic study.[25]

The detailed knowledge of the equilibria and structure of the $Tl(CN)_n(OH_2)_m^{3-n}$ complexes constitutes the basis for a study of ligand exchange dynamics in this system and is a necessary precondition for suggesting reliable reaction mechanisms. The distribution of cyanide among the different species (Figure 1) indicates a considerable stability of the complex $Tl(CN)_2(OH_2)_4^+$, which exists in a wide region of concentrations even in very acidic solutions.

In ^{205}Tl NMR spectra of aqueous solutions in natural isotopic abundance, $Tl(CN)_n^{3-n}$ complexes ($n = 0-4$) give rise to five singlet peaks (*cf.* Figure 1 of ref 7) with no measurable line broadening at room temperature. In ^{205}Tl NMR spectra of ^{13}CN-enriched solutions a very strong ^{13}C−^{205}Tl spin−spin coupling appears (5−15 kHz) offering yet another time scale for dynamic studies.[7]

Recently, ^{205}Tl and ^{13}C NMR 2D-EXSY technique was applied on a ^{13}C-enriched aqueous solution containing the species $Tl(CN)_3$, $Tl(CN)_4^-$, and HCN.[25] From the cross peak pattern it was concluded that the T_1 relaxation time scale of the ^{205}Tl nucleus is suitable for dynamic analysis for the higher complexes. It was also shown that only such exchange reactions occur in which a single cyanide ion jumps between the exchanging sites. For lower complexes, where the ligand exchange appears to be much slower, the carbon-13 T_1 time scale seemed to be promising. In the current paper, we present a systematic kinetic study of ligand exchange in the thallium(III) cyanide system in aqueous solution containing 4 M ionic medium. Since most of the investigated solutions were kept acidic in order to prevent the hydrolysis of Tl(III), HCN had to be considered as one of the possible exchange partners. The

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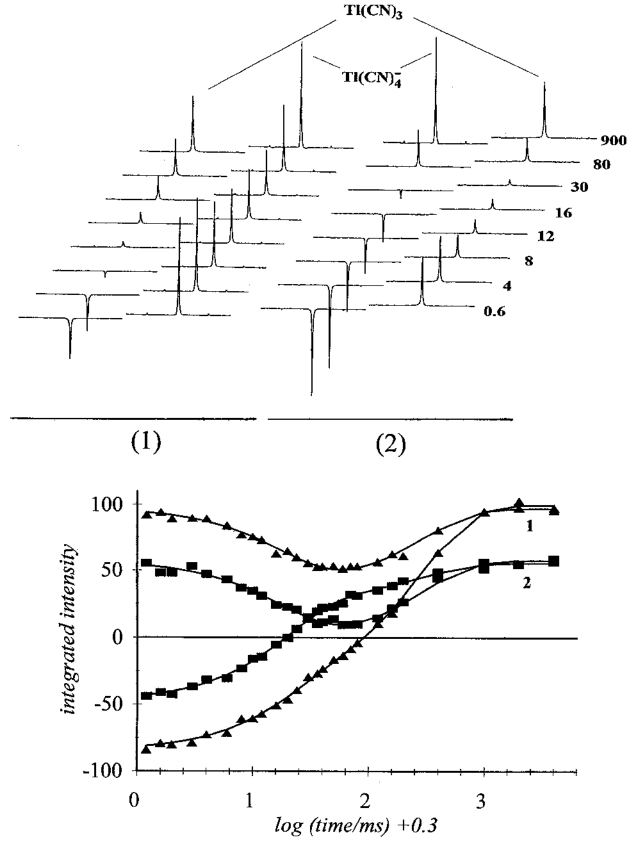

Figure 2. (a) Top: Typical magnetization transfer experiments in ^{205}Tl NMR. The left side (1) shows the inversion of the $Tl(CN)_3$ signal (while observing the $Tl(CN)_3$ and $Tl(CN)_4^-$ signals), and the right side (2) shows the inversion of the $Tl(CN)_4^-$ signal. The numbers represent the delay in milliseconds between the selective π-pulse and the "reading" $\pi/2$-pulse. (b) Bottom: Illustration of the result of parameter fitting using eq 3. Curves 1 belong to $Tl(CN)_4^-$ while curves 2 belong to $Tl(CN)_3$.

study was performed using the ^{205}Tl and ^{13}C NMR 1D inversion transfer technique. The one-dimensional technique was applied because in the case of a few signals 2D-experiments would be more time-consuming and the results would probably be less precise.[30,31] The obtained dynamic information is discussed and compared to the corresponding data for the thallium(III) halide complexes.

Experimental Section

Preparation and Analysis of Solutions. A ~1.4 M aqueous stock solution of $Tl(ClO_4)_3$ in 3.8 M $HClO_4$ was prepared by anodic oxidation of $TlClO_4$ solution.[32,33] The samples were prepared from the appropriate volume of the diluted stock solution, the solutions of 4 M $HClO_4$, 4 M $LiClO_4$, and 4 M $NaClO_4$, and a weighted amount of solid NaCN. In order to keep the activity coefficients of the reacting species constant, the total perchlorate concentration was kept at 4 M and $[Na^+]_{tot}$ at 1 M, whereas $[Li^+]_{tot}$ and $[H^+]_{tot}$ were varied[34] depending on the desired solution composition.

The acid content and the thallium content of the stock solution were determined as described elsewhere.[35] The composition of the samples was determined by quantitative ^{205}Tl NMR. Some details of sample preparation and analysis were described in the previous paper.[23]

NMR Measurements. All NMR spectra were recorded at a probe temperature of 25 ± 0.5 °C with a Bruker AM400 spectrometer. The magnetic field was unlocked; field drift was found to be negligible.

Thallium-205 NMR. Spectrometer frequency = 230.8 MHz, flip angle ≈ 15° (15 μs), and the pulse repetition time varied between 0.02 and 0.5 s depending on the solution composition since the relaxation rates for the different complexes were different. The chemical shifts are reported in ppm toward higher frequency with respect to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution.

Carbon-13 NMR. Spectrometer frequency = 100.6 Mhz, flip angle ≈ 30° (8 μs), and the relaxation delay was in the range 4−16 s depending on the relaxation rates of the investigated species. The chemical shifts are reported in ppm toward higher frequency with respect to an external water-soluble sodium derivative of TMS.

Inversion Recovery Experiments. A microprogram was written on an Aspect 3000 computer for application of the "*relaxation delay*−π (selective)−variable delay−$\pi/2$−aquisition" pulse sequence, with regulation of the frequency offset exactly on the observed peaks in order to obtain quantitative spectra. The 90° ($\pi/2$) pulse length was determined for solutions with varying acidity. In the case of ^{205}Tl NMR there was no need to apply a selective π pulse because the applied pulse was soft enough (160−200 μs) and thus affected only the peak on resonance. In ^{13}C NMR, a 40 element DANTE pulse sequence was applied in order to achieve a selective inversion of the desired peaks.[36,37] Integrated intensities were determined by using the standard Bruker software. In the majority of cases the complementary experiments were also carried out; i.e., both peaks vere inverted resulting in four series of experimental points (Figure 2a).

Results and Calculations

Data Treatment. A typical inversion-transfer experiment for a two-site exchange case is shown in Figure 2a. The calculations were made on the basis of the explicit equation suggested by Led and Gesmar,[31] which can be written as

$$\mathbf{M} = \mathbf{C}\exp(-\lambda t) + M^{\infty} \qquad (3)$$

where **M** is the column matrix of magnetization, **C** is a square matrix, and $\exp(-\lambda t)$ is the column matrix of constants. The constants are combinations of eight parameters written below, while t is the delay time between the selective inversion pulse and the nonselective, reading pulse (*cf.* Supporting Information).

When the complementary experiments were run, the four curves were handled together as shown in Figure 2b. In most of the experiments the following eight parameters were refined using a homemade program based on the Gauss−Newton−Marquardt algorithm: pseudo-first-order rate constants, k_A and k_B, longitudinal relaxation rates, R_{1A} and R_{1B}, and the equilibrium and the initial magnetizations at both exchanging sites, M_A^{∞}, M_A^0, M_B^{∞}, and M_B^0. (Ideally, $|M_i^{\infty}| = |M_i^{\mathbf{0}}|$, but the used way of calculation eliminates the effect of a nonperfect selective inversion.) When one of the relaxation rates was available from independent experiments, it was kept constant in order to obtain lower standard deviations for the rate constants.

In two cases we faced a situation when one or more species in the solution had much shorter relaxation times than the other. It carried two consequences. First, when the signal with fast relaxation rate was inverted, no magnetization transfer was observed because the longitudinal magnetization of the inverted signal relaxed before being transferred by chemical exchange to the other sites. In this case a determination of the pseudo-first-order rate constants was not possible. Secondly, when the signal was inverted which had an appropriately long relaxation

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time compared to the exchange rate, no magnetization transfer could be observed on the other signals either. This can be explaned in the following way. Consider a simple model of three site exchange between the sites A, B, and C:

$$\begin{array}{ccccc} A & \underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} & B & \underset{k_{CB}}{\overset{k_{BC}}{\rightleftharpoons}} & C \\ \downarrow R_A & & \downarrow R_B & & \downarrow R_C \end{array} \qquad (4)$$

If we put negative magnetization on peak B, the magnetization from site B has three possible paths to leak away from the system: (1) R_B, (2) k_{BA} followed by R_A, and (3) k_{BC} followed by R_C. Thus, it will apparently relax with the following rate:

$$\frac{dM_z}{dt} = -(R_B + k_{BA} + k_{BC})M_z = -RM_z \qquad (5)$$

Therefore, the rate-determining step for leaking of magnetization on sites A and C is the chemical exchange. If we determine the apparent relaxation rate for site B at different solution compositions, the values of k_{BA} and k_{BC} can be determined from the concentration dependence using nonlinear least-squares analysis. If R_A and R_C are much larger than k_{AB} and k_{CB}, respectively, no transfer of negative magnetization can be observed.

(i) Determination of the Rate Equations by Means of ^{205}Tl NMR. (a) Exchange between $Tl(CN)_3(OH_2)$ and $Tl(CN)_4^-$. Considering the equilibrium parameters, a series of solutions could be prepared in which only the third and fourth complexes were present with varying relative population. This was achieved by changing the acid concentration and keeping the other concentrations constant. Successful inversion transfer experiments were carried out; the relaxation rates and pseudo-first-order rate constants were determined as described above; *cf.* Figure 2. The pseudo-first-order rate constants are shown as a function of the molar fractions of the exchanging complexes in Figure 3.

It can be seen that k_{43}^{obs} is linearly dependent on the molar fraction of the third complex, p_3, and hence also on p_4, since $p_3 = (1 - p_4)$. Two exchange paths which can transfer magnetization from $Tl(CN)_4^-$ to $Tl(CN)_3$ are potentially observable in ^{205}Tl NMR spectra:

$$Tl(CN)_4^- \underset{k'_{34}}{\overset{k'_{43}}{\rightleftharpoons}} Tl(CN)_3 + CN^- \qquad (6)$$

$$Tl(CN)_4^- + Tl(CN)_3{}^- \overset{k_{43}}{\rightleftharpoons} Tl(CN)_4^- + Tl(CN)_3 \qquad (7)$$

For reactions 6 and 7, the rate equation would be

$$\text{rate} = k'_{43}[Tl(CN)_4^-] + 2k_{43}[Tl(CN)_4^-][Tl(CN)_3] \qquad (8)$$

Multiplication by 2 in the second term of eq 8 is necessary because in eq 7 both directions must be considered, and $k_{43} = k_{34}$. Hence,

$$\frac{\text{rate}}{[Tl(CN)_4^-]} = k_{43}^{obs} = k'_{43} + 2k_{43}[Tl]_{tot}p_3 = k'_{43} + 2k_{43}[Tl]_{tot}(1 - p_4) \qquad (9)$$

When the total thallium concentration is constant, this expression shows a linear dependence of k_{43}^{obs} on p_4, as represented by curve 1 in Figure 3.

According to the principle of microscopic reversibility, the opposite reaction paths, and *only* the opposite ones, should also exist. However, the rate of the opposite reaction does not give a linear dependence on p_4. The following short deduction leads to the equation which describes the dependence of k_{34}^{obs} on p_4:

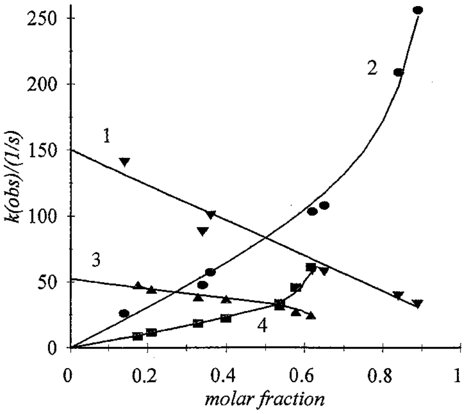

Figure 3. Dependence of k_{43}^{obs} (1) and k_{34}^{obs} (2) on the thallium molar fraction of the $Tl(CN)_4^-$ complex (p_4) and of k_{32}^{obs} (3) and k_{23}^{obs} (4) on the molar fraction of the $Tl(CN)_3$ complex (p_3). $[Tl]_{tot} = 0.15$ M, $[CN^-]_{tot} = 1$ M, and $[H^+]_{tot}$ varies as shown in Figure 1. The solid lines are the calculated curves from the best fit using eqs 9, 13, and 17, 18.

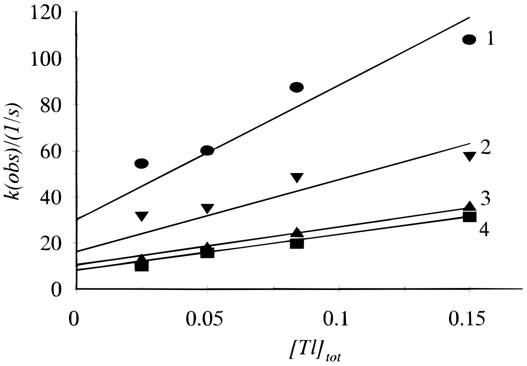

Figure 4. Dependence of k_{34}^{obs} (1), k_{43}^{obs} (2) ($p_4 = 0.65$) and k_{32}^{obs} (3), k_{23}^{obs} (4) ($p_3 = 0.56$) on the total concentration of thallium. The solid lines are calculated from the best fit using eqs 9, 13, and 17, 18 and all experimental data points (see text).

$$\text{rate} = k'_{34}[Tl(CN)_3][CN^-] + 2k_{34}[Tl(CN)_3][Tl(CN)_4^-] \qquad (10)$$

$$\frac{\text{rate}}{[Tl(CN)_3]} = k_{34}^{obs} = k'_{34}[CN^-] + 2k_{34}[Tl]_{tot}p_4 \qquad (11)$$

$[CN^-]$ can now be expressed by introduction of K_4, the stepwise stability constant of $Tl(CN)_4^-$, as follows:

$$K_4 = \frac{[Tl(CN)_4^-]}{[Tl(CN)_3][CN^-]} = \frac{p_4}{(1 - p_4)[CN^-]} \qquad (12)$$

Therefore, k_{34}^{obs} is

$$k_{34}^{obs} = \frac{k'_{34}p_4}{K_4(1 - p_4)} + 2k_{34}[Tl]_{tot}p_4 \qquad (13)$$

The plot of k_{34}^{obs} *vs* p_4 is shown as curve 2 in Figure 3. Furthermore, eqs 9 and 13 show a linear dependence of k_{34}^{obs} and k_{43}^{obs} on $[Tl]_{tot}$ if p_4 is constant. These equations are plotted as curves 1 and 2, respectively, in Figure 4.

A nonlinear parameter fitting procedure was applied using eqs 9 and 13 on 19 measured points (each point originates from four kinetic curves) from the experiments at different total thallium concentrations with variable ratio between the third and fourth complexes. In order to improve the fitting, only two parameters were refined resulting in $k_{34} = k_{43} = 446 \pm 14$ M^{-1} s^{-1} and $k'_{43} = k'_{34}/K_4 = 16.3 \pm 1.5$ M^{-1} s^{-1}, from which $k'_{34} = 4.48 \times 10^8$ M^{-1} s^{-1} because $K_4 = 2.75 \times 10^7$.[7] The solid lines in Figures 3 and 4 represent the results of parameter fitting of all experimental data.

(b) Exchange between $Tl(CN)_2(OH_2)_4^+$ and $Tl(CN)_3(OH_2)$. The next series of solutions were prepared by increasing the acidity but not changing the other concentrations; the dominant species were the second and third complexes (*cf.* Figure 1). A much less pronounced inversion transfer was observed in this case indicating a slower exchange process. Curves 3 and 4 in Figures 3 and 4 show the dependence of the pseudo-first-order rate constants on p_3 and $[Tl]_{tot}$. The following exchange reactions were considered in order to describe these changes:

$$Tl(CN)_2^+ + CN^- \underset{k'_{32}}{\overset{k'_{23}}{\rightleftharpoons}} Tl(CN)_3 \tag{14}$$

$$Tl(CN)_2^+ + Tl(CN)_4^- \underset{k_{33}}{\overset{k_{24}}{\rightleftharpoons}} 2Tl(CN)_3 \tag{15}$$

$$Tl(CN)_2^+ + Tl(CN)_3 \underset{k_{23}}{\overset{k_{32}}{\rightleftharpoons}} Tl(CN)_2^+ + Tl(CN)_3 \tag{16}$$

In the same way as above (eqs 8 and 9 and 10−13), the following equations were constructed in order to describe the dependence of the pseudo-first-order rate constants on p_2, p_3, and $[Tl]_{tot}$ using the relation $p_4 = 1 - p_2 - p_3$.

$$k_{23}^{obs} = \frac{k'_{23} p_3}{K_3 p_2} + k_{24}[Tl]_{tot}(1 - p_2 - p_3) + 2k_{23}[Tl]_{tot} p_3 \tag{17}$$

$$k_{32}^{obs} = \frac{k'_{23}}{K_3} + k_{24}\frac{\beta_4\beta_2}{\beta_3^{\,2}}[Tl]_{tot} p_3 + 2k_{32}[Tl]_{tot} p_2 \tag{18}$$

A measurable amount of the fourth complex was present only in three samples but always less than 10% of the total thallium concentration. In these three cases the pseudo-first-order rate constants were calculated on the basis of a three-site exchange model using the previously determined rate constants for the third and fourth complexes as fixed parameters. Again, the connections between the rate constants were extracted from the microscopic reversibility, *i.e.* $k_{33} = k_{24}(\beta_4\beta_2/\beta_3^2)$, $k'_{23} = k'_{32}K_3$ and $k_{23} = k_{32}$. These three rate constants were calculated: $k'_{32} = 7.3 \pm 1.4$ M^{-1} s^{-1} ($k'_{23} = 3.43 \times 10^9$ M^{-1} s^{-1}, $K_3 = 4.7 \times 10^{8}$ [7]), $k_{24} = 712 \pm 200$ M^{-1} s^{-1}, and $k_{23} = 161 \pm 9$ M^{-1} s^{-1}. The constant k_{24} is determined by only a few points; thus, its calculated standard deviation has limited statistical significance.

(c) Exchange between Lower Complexes ($n \leq 2$). In order to investigate the dynamics of lower complexes it was necessary to decrease the ligand-to-metal ratio; otherwise, no dominance of the monocyano complex or aqua complex could be achieved (*cf.* Figure 1). However, at low ligand-to-metal ratios no inversion transfer was observed at room temperature. After the 180° pulse, the signals of $Tl(CN)^{2+}$ and $Tl(CN)_2^+$ relaxed independently with their own relaxation rates. Apparently, their relaxation times, 30 ms (*i.e.* relaxation rate constant ≈ 30 s^{-1}) and 20 ms (50 s^{-1}), respectively, are too short compared to the rate of the exchange reaction at room temperature. Hence, supposing that a 10% change in the magnetization through chemical exchange would be detectable in the presence of the longitudinal relaxation, the upper limit of the pseudo-first-order rate constant is about 3−5 s^{-1}. On the other hand, the long relaxation time of the $Tl(OH_2)_6^{3+}$ complex, $T_1 = 1.2$ s ($R_{aq} = 0.83$ s^{-1}), could provide a time scale for studying of exchange reactions involving lower complexes. Thus, the relaxation rate of the aqua complex was now measured in the presence of the $Tl(CN)^{2+}$ and $Tl(CN)_2^+$ complexes and evaluated according to eq 5. The R^*_{aq} value showed a linear dependence on p_2 (molar fraction of the second complex), which may be attributed to the following exchange reaction:

$$Tl^{3+} + Tl(CN)_2^+ \underset{k_{11}}{\overset{k_{02}}{\rightleftharpoons}} 2Tl(CN)^{2+} \tag{19}$$

The slope of R^* *vs* p_2 is 0.49 ± 0.02 s^{-1}, from which $k_{02} = 4.1 \pm 0.3$ M^{-1} s^{-1} while the intercept, $R_{aq} = 0.861$, is in excellent agreement with the determined relaxation rate in the absence of cyanide ligands.

^{205}Tl NMR did not provide any additional way to obtain rate constants for the other possible exchange reactions. From these data, one can calculate an upper limit for the rate constant of exchange for the reaction type 1 between the aqua complex and first cyano complex. We assume that the pseudo-first-order rate constant of this exchange may not be larger than 10% of R_{aq}, that is 0.08 s^{-1} at the highest used concentration of $Tl(CN)^{2+}$ (about 0.03 M in these experiments). From this, $k_{01} = 0.08/0.03 = 2.6$ M^{-1} s^{-1} is a possible upper limit.

(ii) Determination of Rate Equations by Means of ^{13}C NMR. ^{13}C NMR spin−lattice relaxation times in the studied system are much longer than those in ^{205}Tl NMR. This has allowed one to investigate slower exchange processes using magnetization transfer between the cyanide ligands of the ^{13}C-enriched complexes.

Exchange Reactions Involving $Tl(CN)(OH_2)_5^{2+}$ and $Tl(CN)_2(OH_2)_4^+$. In order to investigate the self-exchange reaction between the first and second complex, samples were prepared for which ^{13}C NMR spectra showed only signals of these two species. Even if small amounts of Tl_{aq}^{3+} were unavoidable, it did not disturb the conclusions. The coupled doublet of $Tl(CN)_2(OH_2)_4^+$ in the ^{13}C NMR spectrum was inverted by means of two side bands of a DANTE pulse sequence, but it was found that it relaxed with the time constant $R \approx 0.5$ s^{-1} ($T_1 \approx 2$ s), independently of the composition of the samples. Taking into account that in case of a 10% contribution the transfer of magnetization should have been detected, an upper limit of 0.05 s^{-1} was estimated for the first-order rate constant of the exchange reaction type 1 between the first and the second complex. In this solution the concentration of first complex was 0.05 M; thus, the upper limit of $k_{12} = k_{21}$ is ~1 M^{-1} s^{-1}. The highest value of k'_{12} could not be estimated because of the very low concentration CN^-.

Since T_1 of the ^{13}C nucleus in HCN could be determined from independent experiments and was found to be considerably longer ($T_1 = 16.3$ s), it could allow an estimation of $k_{HCN,1}$, that is the transfer of CN^- from HCN to $Tl(CN)^{2+}$. Unfortunately, samples containing the complexes $Tl(OH_2)_6^{3+}$ and $TlCN(OH_2)_5^{2+}$ in the presence of HCN, in concentrations measurable by ^{13}C NMR, could not be prepared because of the high stability of $Tl(CN)_2^+$. Consequently, no data could be recorded and no reliable limits for k'_{01} and k'_{12} could be determined in this way.

In the case of the second complex, solutions could be prepared containing exlusively HCN and $Tl(CN)_2^+$ in a wide variety of concentration of the second complex. In Figure 5, a series of ^{13}C-NMR inversion transfer experiments from the HCN doublet to the $Tl(CN)_2^+$ doublet are shown. A 300 Hz broad "selective" pulse train was constructed by which the HCN doublet could be inverted with at least 80% efficiency. Although these

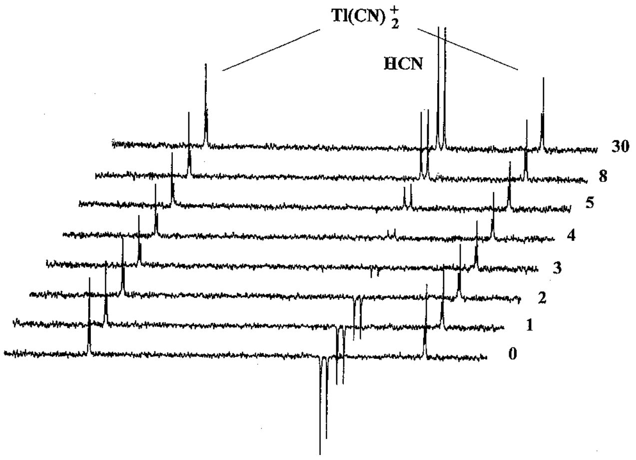

Figure 5. ^{13}C NMR inversion transfer between HCN and $Tl(CN)_2^+$, in the case when the inversion transfer had a visible effect on the signal of $Tl(CN)_2^+$. The variable delay time in seconds between the selective π-pulse and the "reading" $\pi/2$-pulse is shown.

experiments do not concern ligand exchange between the various thallium sites and are principally outside the scope of this work, we considered them necessary for the discussion of the mechanism of the anation reactions (see Discussion). Depending on the concentrations, a transfer of the inverted magnetization was or was not observed but in all cases the apparent spin−lattice relaxation time of HCN was shorter than in the absence of Tl(III). When measurable inversion transfer was found, eq 3 was used for calculating the pseudo-first-order rate constants $k^{obs}_{HCN,2}$ and $k^{obs}_{2,HCN}$. When the effect appeared only in the relaxation time T_1 of HCN, then eq 5 was used to calculate $k^{obs}_{HCN,2}$, and $k^{obs}_{2,HCN}$ was calculated using the microscopic reversibility from the known composition of the solution. $k^{obs}_{HCN,2}$ showed a linear dependence on the $Tl(CN)_2^+$ concentration (intercept = 0) and was not dependent on the HCN equilibrium concentration. $k^{obs}_{2,HCN}$ gave the opposite dependence from which the following exchange path could be identified:

$$Tl(^*CN)_2{}^+ + HCN \underset{k^*_{HCN,2}}{\overset{k^*_{2,HCN}}{\rightleftharpoons}} Tl(CN)_2{}^+ + H^*CN \qquad (20)$$

From linear plots of $k^{obs}_{HCN,2}$ *vs* $[Tl(CN)_2^+]$ and $k^{obs}_{2,HCN}$ *vs* [HCN], the second order rate constants at 1.4 M acid concentration are $k^*_{HCN,2} = 1.7 \pm 0.16$ and $k^*_{2,HCN} = 0.76 \pm 0.14$ M^{-1} s^{-1}. Since one molecule of $Tl(CN)_2^+$ contains 2 CN$^-$ ligands, we obtain

$$\text{rate} = \frac{d[HCN]}{dt} = k^*_{HCN,2}[HCN][Tl(CN)_2{}^+] = -\frac{1}{2}\frac{d[Tl(CN)_2{}^+]}{dt} = k^*_{2,HCN}2[Tl(CN)_2{}^+][HCN] \qquad (21)$$

From the equality of the rate in both directions, it follows that $k^*_{HCN,2} = 2k^*_{2,HCN}$ in agreement with the experimental finding. We have also found out that $k^{obs}_{HCN,2}$ decreases with increasing acid concentration (*cf.* Figure S7 in Supporting Information); consequently, the same is true for the second-order rate constants $k^*_{HCN,2}$ and $k^*_{2,HCN}$. The following equation could be fitted to the experimental data of Figure S7:

$$k^{obs}_{HCN,2} = k'_2 + k'_1/[H^+] \qquad (22)$$

with $k'_2 = 0.037 \pm 0.003$ s^{-1} and $k'_1 = 0.046 \pm 0.004$ M s^{-1}. From this, we conclude that in the reaction path (20), also the following parallel exchange path seems to be operative:

$$Tl(^*CN)_2{}^+ + CN^- \underset{k_{CN^-,2}}{\overset{k_{2,CN^-}}{\rightleftharpoons}} Tl(CN)_2{}^+ + {}^*CN^- \qquad (23)$$

Since the total concentration of cyanide is equal to $c_{HCN} = [CN^-] + K_p[H^+][CN^-]$, where $K_p = [HCN]/[H^+][CN^-] = 1.29 \times 10^{10}$ M,[38,39] the equilibrium concentration of CN$^-$ can be calculated as $[CN^-] = c_{HCN}/K_p[H^+]$, because $K_p[H^+] \gg 1$, and $[HCN] \approx c_{HCN}$. Thus, the total rate of cyanide exchange for the $Tl(CN)_2^+$ complex can be obtained by considering eqs 20 and 23:

$$\text{rate} = 2k_{HCN,2}[Tl(CN)_2{}^+][HCN] + 2k_{CN^-,2}[Tl(CN)_2{}^+][CN^-] \qquad (24)$$

After substitution of [CN$^-$] and [HCN],

$$\frac{\text{rate}}{c_{HCN}} = k^{obs}_{HCN,2} = \left(2k_{HCN,2} + \frac{2k_{CN^-,2}}{K_p[H^+]}\right)[Tl(CN)_2{}^+] \qquad (25)$$

we get an equation which has the same form as eq 22, since $[Tl(CN)_2^+]$ is constant in the studied solutions. Using this equation, $k_{CN^-,2} = k'_1K_p/2[Tl(CN)_2] = 0.046 \times 1.29 \times 10^{10}/2 \times 0.05 = 6(\pm 0.5) \times 10^9$ M^{-1} s^{-1}, while $k_{HCN,2} = 0.37(\pm 0.03)$ M^{-1} s^{-1}. Note, that $k^*_{HCN,2}$ is used for the total exchange process (i.e. both for the reaction of $Tl(CN)_2^+$ with HCN and with CN$^-$) and $k_{HCN,2}$ when only the exchange path with contribution of HCN is considered.

The kinetic data obtained for the cyano complexes, together with the corresponding data obtained previously for the halide complexes, are summarized in Table 1. Calculation of rate constants of the rate-determining steps is model-dependent and it is dealt with in the Discussion section.

Discussion

Ligand Exchange between Complexes. Similarly to the thallium(III) halide complexes,[23,24] also in the case of cyanide ligands the ligand exchange is dominated by reactions occurring via a direct encounter of two complexes (*cf.* eqs 7, 15, 16, and 19). In the following, we will call this reaction type *ligand self-exchange* between complexes, in analogy to electron self-exchange reactions.[40] For such reactions Scheme 1 can be written (here exemplified by reaction k_{23}).

Scheme 1 differs from the usual picture of ligand exchange processes because the "incoming ligand" is also a complex. It shows a reaction in which each of the consecutive steps could be rate-determining; certainly, this is a simplification of a concerted mechanism in which the exchange constitutes a continuum moving from one outer-sphere complex to another. The first step, the formation of the outer-sphere complex, is assumed to be diffusion-controlled and is considered as a pre-equilibrium. The value of the equilibrium constant, K_{os}, may be estimated by the Fuoss equation[41,42] considering only electrostatic interactions between the species encountered. For the reaction paths characterized by k_{23} and k_{34}, $K_{os} = 0.3$ M^{-1} (one of the exchange partners is neutral), while $K_{os} = 1.3$ (+,−) and 5×10^{-3} (3+,+) for k_{24} and k_{02}, respectively.

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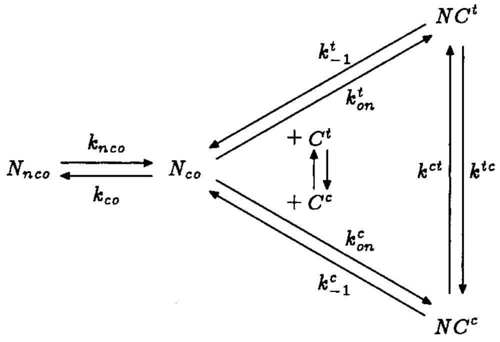
Scheme 1

$$k_{\mathrm{nco}} = 2 \times 10^{-3}\mathrm{s}^{-1} \qquad k^{c}_{-1} = 3.4 \times 10^{-5}\mathrm{s}^{-1}$$

$$k_{\mathrm{co}} = 1.6 \times 10^{-3}\mathrm{s}^{-1} \qquad k^{tc} = 4 \times 10^{-3}\mathrm{s}^{-1}$$

$$k^{t}_{\mathrm{on}} = 1.2 \times 10^{3}\mathrm{M}^{-1}\mathrm{s}^{-1} \qquad k^{c}_{\mathrm{on}} = 2.5 \times 10^{3}\mathrm{M}^{-1}\mathrm{s}^{-1}$$

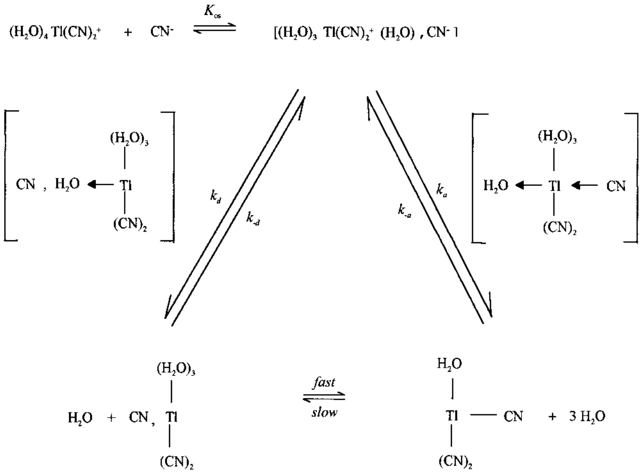
$$k^{ct} = 2.1 \times 10^{-4}\mathrm{s}^{-1} \qquad k^{t}_{-1} = 3 \times 10^{-3}\mathrm{s}^{-1}$$



The next step is a formation of an intermediate/transition state. The equilibrium constant is $K_f = k_f/k_{-f}$. The gain from the introduction of this second equilibrium constant is simply that we take into account the chemical nature of the reactants. For example, in the case of a bidentate ligand a bridge evidently provides higher stability than a simple electrostatic interaction, or if several potentially bridge-forming ligands are present, then the probability of a proper orientation is larger.[30,43] Unfortunately, there is no formula to calculate this constant. In the following discussion, we assume that $K_f = 1$.

If we suppose that one of the first-order steps following the equilibria characterized by K_{os} and K_f is rate-determining, then the rate constant for this step can be calculated as $k^{\mathrm{rds}}_{mn} = k_{mn}/(K_{os}K_f)$. The obtained values are given in Table 1, together with the values determined earlier for the thallium(III) halide complexes.[23,24] In the case of the halide complexes the reported data are in accordance with an I_d-type mechanism; that is, the rate-determining step is the leaving of a coordinated water molecule from the ion pair (k_a in Scheme 1). If the rate-determining step is the Tl-O bond rupture, its rate can be expected to be similar for the halide and for the cyano complexes. (In fact, the Tl−OH$_2$ distances in the cyano complexes (2.42 Å) are significantly longer than the corresponding distances in the halo complexes (2.21−2.37 Å);[14] hence, the Tl-O bond breaking in $\mathrm{Tl(CN)}_n(\mathrm{OH}_2)_m{}^{3-n}$ could be much faster.) The calculated k^{rds}_{mn} values for cyano complexes (Table 1) are at least 3 orders of magnitude smaller; therefore, this mechanism is less probable in this case. Rather, the apparent uniformity of the k^{rds}_{mn} values for the cyano complexes indicates that the rearrangement of the intermediate, that is the rupture of a Tl-C bond, is the rate-determining step (k_r in Scheme 1). In fact, a flip-over of a bridging cyanide has been reported to be measurably slow for $[\mathrm{Mn_2H(CN)(CO)_4(dppm)_2}]$ at −75 °C,[44,45] which would make an estimate of ~10^4 flips/s at +25 °C. Comparing these results with those for the halide complexes, we can conclude that the rupture of a Tl−X bond (where X = Cl$^-$ or Br$^-$) is fast and the rupture of a Tl−O bond (coordinated water) is slower, while the Tl−C bond is very inert. Recently, the Tl−CN bond dissociation was found to be slower then 3 s^{-1} in the Tl(edta)CN^{2-} complex;[46] this is in accordance with our conclusion although the large chemical difference between the presently studied complexes and Tl(edta)(CN)$^{2-}$ is apparent. Therefore, we state that the above order of reactivity is in accordance with the high stability of the Tl(III) cyano complexes[7] and with the fact that the Tl−CN bond is different in nature.[47] The Tl−C bonds are ~0.3 Å shorter than the Tl−X bonds in the halide complexes.[14]

Scheme 2



The only k^{rds}_{mn} value which may differ from the others is k^{rds}_{12}. The same situation occurs for the chloro and bromo complexes (see Table 1). Possibly, the highly symmetrical transition state complex can be an explanation, in the same way as the TlX$_2{}^+$ complexes show an exceptional thermodynamic[3,4,7] and structural[14] stability.

Anation Reactions. The anation reactions, characterized by k'_{mn}, could follow two alternative reaction paths; *cf.* Scheme 2. The left side of Scheme 2 represents the dissociative interchange mechanism in which the rate-determining step is the leaving of a coordinated water molecule. The right side shows an associatively activated anation reaction. For anation reactions only two rate constants, k'_{23} and k'_{34}, could be determined.

As shown in Table 1, for these reaction paths the second-order rate constants k'_{mn} are almost identical independently of the type of the ligands (except for k'_{12} for the chloride case) even if these are as different as cyanide and halides (*cf.* Table 1 and ref 24). For all the $\mathrm{TlX}_n{}^{3-n}$ complexes (X = Cl, Br,

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CN), the rates determined for this reaction type are close to the diffusion-controlled limit.[24] Suppose that the formation of the outer-sphere complex is diffusion-controlled; that is, the rate constant is 10^9−10^{10} $\mathrm{M^{-1}\ s^{-1}}$.[48] The rate of diffusion for the studied reactions is

$$\mathrm{rate}_{34}^{\mathrm{diff}} = k_{\mathrm{diff}}[\mathrm{Tl(CN)_3}^+][\mathrm{CN}^-]$$
$$\mathrm{rate}_{23}^{\mathrm{diff}} = k_{\mathrm{diff}}[\mathrm{Tl(CN)_2}^+][\mathrm{CN}^-] \qquad (26)$$

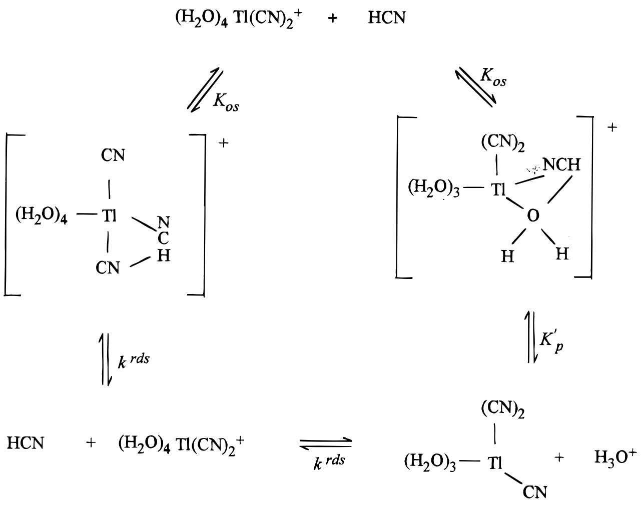
Thus, the second-order rate constants can directly be compared to the diffusion rate constant. The constant $k'_{34} = 4.5 \times 10^8$ $\mathrm{M^{-1}\ s^{-1}}$ may be considered lower than k_{diff}, but $k'_{23} = 3.4 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$ is probably diffusion-controlled. The latter is also valid for the corresponding thallium bromide anation reactions ($k'_{34} = 1.5 \times 10^9$, $k'_{23} = 5.6 \times 10^{10}$ $\mathrm{M^{-1}\ s^{-1}}$), but not the chloride case ($k'_{34} = 4.7 \times 10^8$, $k'_{23} = 1.3 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$).[24]

We can now compare the calculated k'^{rds}_{mn} values of anation for the different ligands. The values are very high for all three ligands ($\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{CN^-}$) and differ by not more than 2 orders of magnitude. The cyanide ligand behaves quite differently from the halides in the self-exchange reactions (*cf.* Scheme 1), but this difference is not pronounced in the anation reactions. As shown in the left side of Scheme 2, the dissociative reaction path would include a dissociation of a water molecule from the thallium complex. The expected rate constant for this dissociation is $\sim 10^7$ $\mathrm{s^{-1}}$, as previously determined for the corresponding chloro and bromo complexes.[24] Hence, since the rate constants, k^{rds}, determined for all anation reactions are significantly larger than this value (see Table 1), the dissociative interchange mechanism can be excluded.

For the associatively activated mechanism the water molecule in the transition state complex (right side of Scheme 2) should be labilized by the increased coordination number of the thallium atom. We could expect that this labilizing effect will vary for the different ligands. But such a variation would certainly be much less characteristic for a specific ligand than is the Tl−X bond breaking in the self-exchange reactions. The situation is somewhat confusing because the diffusion may also be the rate-determining step for some of the anation reactions, e.g. k'_{23} for the bromo complexes (see above). In the case of $\mathrm{Tl(edta)(OH_2)^-}$ complex, anation reactions by bromide, chloride, thiocyanate, and cyanide were recently studied.[46] The determined rate constants of the rate determining steps were found to be $\sim 10^8$ $\mathrm{s^{-1}}$, although the limiting values were estimated to fall in the range between 10^6 and 10^{10} $\mathrm{s^{-1}}$. This shows that the labilizing effect of different ligands does not differ much.

Ligand Substitution Reactions. In the case of cyanide complexes (in contrast to the chloro and the bromo complexes) the availability of the second NMR active nucleus, namely $^{13}\mathrm{C}$, allowed detection of ligand substitution reactions without net chemical exchange, *i.e.* eqs 20 and 23. For the complex $\mathrm{Tl(CN)_2^+}$, we have determined two possible parallel exchange paths, $k_{\mathrm{HCN},2}$ and $k_{\mathrm{CN^-},2}$ (eq 24). The second-order rate constant for the exchange with $\mathrm{CN^-}$, $k_{\mathrm{CN^-},2} = 6 \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$, is very close to 10^{10} (diffusion limit). The possible mechanism is very similar to that outlined in Scheme 2 (right side), but all steps which follow the diffusion ($K_{\mathrm{os}} = k_{\mathrm{diff}}/k_{-\mathrm{diff}}$) may have higher rate than the diffusion. However, this is a reaction without a net stoichiometrical change; therefore, the terminating step is the dissociation of one cyanide. The latter step is denoted as "slow" because the results for the ligand self-exchange reactions (Scheme 1) showed that the rupture of the Tl−C bond is slow.

Scheme 3



The rate constant k^{rds}_{23} is about 550 $\mathrm{s^{-1}}$ for the corresponding ligand self-exchange reaction and is expected to be approximately the same also in the present case. The rate constant of the rate-determining step can be calculated from $k_{\mathrm{CN^-},2}$ as follows. The experimentally determined rate constant, $k_{\mathrm{CN^-},2} = k^{\mathrm{rds}}K_{\mathrm{os}}$. Since $K_{\mathrm{os}} = 1.3$ M, thus $k^{\mathrm{rds}} = 4 \times 10^9$ $\mathrm{s^{-1}}$ which is not compatible with the value of 550 $\mathrm{s^{-1}}$ obtained from the ligand self-exchange reactions.

These considerations stimulated us to propose an alternative mechanism in which HCN is involved instead of $\mathrm{CN^-}$, still keeping in mind the acid dependence represented by eq 22. First, two types of outer-sphere complexes may be formed with HCN, shown as H-bridge bonded intermediates in Scheme 3. The rearrangement of these species is complicated: many steps may occur, and practically no information is available. The difference between the two intermediates is in the position of HCN.

Assume that the approaching HCN molecule orients itself toward a coordinated water and gives a proton to it. This can be treated as an equilibrium characterized by the protonation constant K'_{p}, resulting in a fast leaving of hydroxonium ion and formation of $\mathrm{Tl(CN)_3}$. Then the dissociation of another $\mathrm{CN^-}$ ligand, supposed to be the rate-determining step, completes the exchange reaction. It leads to the same rate equation as the second term of eq 25. The experimental rate constant is then equal to $k_{\mathrm{CN^-},2} = k^{\mathrm{rds}}K_{\mathrm{os}}/K'_{\mathrm{p}}$; that is, $K'_{\mathrm{p}} = 550 \times 1.3/6 \times 10^9 \approx 10^{-7}$ M. This value is compatible with the perception that the protonated thallium complex is much more acidic than HCN.

If, on the other hand, HCN attacks a coordinated cyanide (left side of Scheme 3), then another $\mathrm{CN^-}$ ligand is pushed out from the coordination sphere of thallium and the proton exchange takes place within the transition state. This path does not give an $[\mathrm{H^+}]$ dependence and may therefore correspond to the first term of eq 25.

Some cyanide exchange reactions where HCN was found to be the more active species have been reported, *e.g.* for the divalent and the trivalent iron complexes $[\mathrm{Fe(CN)_5(OH_2)}]^{2-,3-}$ [49] and for the dimeric species $[\mathrm{Fe_2(CN)_{10}(H_2O)}]^{6-}$.[50] In other cases, *e.g.* for the cyano complexes of gold(I), the $\mathrm{CN^-}$ ion was reactive.[51]

Figure 6 shows the relative contribution of the different parallel exchange paths. It can be seen that the ligand self-exchange between cyano complexes, although slower than that of the halide complexes, is dominant for all ligand to metal

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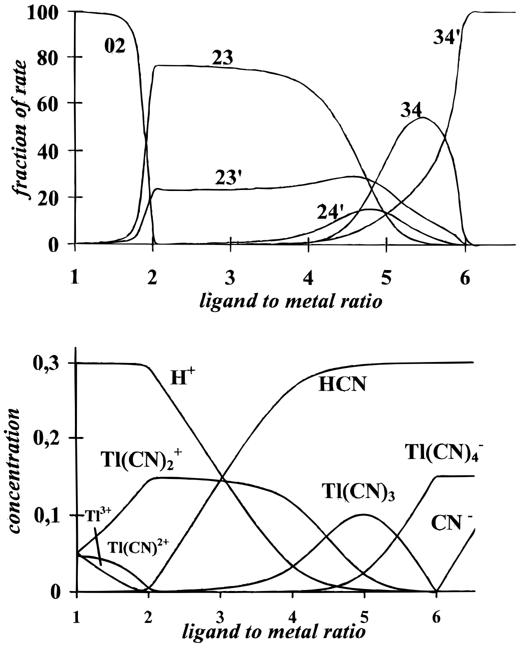

Figure 6. (a) Top: Percentage contribution of different parallel cyanide exchange paths, calculated as $(w_{mn}/\Sigma w_{mn}) \times 100$, to the total exchange rate (Σw_{mn}). (m,n refer to the indices of the rate constants.) $\Sigma w_{mn} = \Sigma\{k_{mn}[\mathrm{Tl(CN)}_m][\mathrm{Tl(CN)}_n] + k'_{mn}[\mathrm{Tl(CN)}_m][\mathrm{CN}^-] + k'_{m,\mathrm{HCN}}[\mathrm{Tl(CN)}_m][\mathrm{HCN}]\}$. $T = 25$ °C. The contribution of the exchange processes determined on the time scale of ^{13}C NMR (eqs 20 and 23) is less than 1%. $[\mathrm{Tl}]_{\mathrm{tot}} = 0.15$ M, and $[\mathrm{H}^+] = 0.3$ M. For the equilibrium distribution of all species in these solutions, see (b) (bottom).

ratios below 6. The reason is the very low concentration of the CN^- ligand and the inertness of the HCN species in the exchange reactions. Having the ^{13}C NMR as an additional tool, some ligand substitution processes became also accessible (eqs 20 and 23). Their contribution is not larger then 1%. The reason that such slow reactions could be observed at all is the very large difference between the ^{205}Tl NMR and ^{13}C NMR time scales.

Conclusions

Our picture of the ligand exchange reactions of thallium(III) complexes in aqueous solution has now been extended. In the cyanide case, for the ligand self-exchange reactions (*e.g.* reactions 7, 15, and 16) breaking of the Tl−CN bond appears to be the rate-determining step, in contrast to the situation found previously for the thallium(III) halide complexes where breaking of the $\mathrm{Tl-OH_2}$ bond determines the reaction rate.[23,24] For the anation reactions, which were also observed in the cyanide system, the rate-determining step is probably a water dissociation mediated by the incoming ligand, an associative interchange mechanism, i.e. similarly to the halide systems. In the case of Tl(III) bromide complexes the anation is probably diffusion-controlled. The choice of the cyanide ligand appeared not to be optimal in order to clarify the mechanistic details of the anation reactions, because of the special feature of cyanide ligand, *i.e.* the formation of the stable and relatively inert HCN. On the other hand, the presence of a second NMR-active nucleus (i.e. ^{13}C) in the studied complexes opened a new possibility, namely the study of the ligand substitution processes according to eqs 20 and 23.

In the light of present results, we can conclude that the multinuclear NMR technique is a powerful tool for investigating not only conformational motion or simple equilibria but also the dynamics of complicated chemical systems with several parallel exchange pathways. In the case of the thallium(III) cyanide system in aqueous solution, it was possible to use a combination of two NMR-active nuclei, one in the center of the complexes (^{205}Tl) and one in the ligand entity (^{13}C). The two NMR techniques complement each other: They not only provide different pieces of information on the reaction pathways but are also sensitive to different time scales due to the different relaxation times (T_1) of these nuclei. For the metal ions of main group III of the periodic table, multinuclear NMR spectroscopy is exceptionally useful for investigation of fast reaction kinetics in solution because other analytical techniques, *e.g.* the commonly used spectrophotometry, are less suitable than for the transition metal complexes.

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Supporting Information Available: Text describing data treatment for inversion-transfer experiments for a two-site exchange case, selected thallium and cyanide distribution diagrams for the studied solutions, and diagrams showing dependence of the relaxation rate of Tl^{3+} on the molar fraction of $\mathrm{Tl(CN)_2}^+$, dependence of the pseudo-first-order rate constants of the reaction between $\mathrm{Tl(CN)_2}^+$ and HCN on the appropriate total concentrations, and dependence of $k^{\mathrm{obs}}_{\mathrm{HCN},2}$ on the acid concentration (5 pages). Ordering information is given on any current masthead page.

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