Complex Formation in the Ternary System Tl(III)−CN^-−Cl^- in Aqueous Solution. A ^{205}Tl NMR Study

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The existence of mixed complexes of the general formula $Tl(CN)_mCl_n^{3-m-n}$ ($m + n \leq 4$) in aqueous solution containing 3 M ionic medium $\{(H^+ + Li^+),ClO_4^-\}$ has been established by means of ^{205}Tl NMR. All six ternary complexes have been identified, and their compositions, chemical shifts, ^{205}Tl−^{13}C spin−spin coupling constants, and peak integrals were determined and used to calculate the stability constants, $\beta = [Tl(CN)_mCl_n^{3-m-n}]/\{[Tl^{3+}][CN^-]^m[Cl^-]^n\}$. Very good agreement was obtained between the equilibrium constants determined in this work and those estimated by a theoretical formula using the stability constants for the binary complexes and a statistical factor. Specific interaction coefficients have been calculated for the $Tl(CN)_m^{3-m}$ ($1 \leq m \leq 4$) complexes. Some interesting correlations were found for the obtained NMR parameters. The stepwise formation constants for addition of one cyanide ligand, log K_{CN}, show linear dependence on both the spin−spin coupling constants, $^1J(^{205}Tl-^{13}C)$, and the chemical shifts, δ_{Tl}. Also the interatomic distance, d(Tl−C), is linearly correlated to the spin−spin coupling constant. The correlations are discussed in terms of the Ramsey equation, involving bond properties, stereochemistry, and stability of the complexes. Since $^1J(^{205}Tl-^{13}C)$ also shows linear dependence on the Tl−CN force constant, it is concluded that the above correlations reflect the Tl−CN bond strength. Thus, the most important factor contributing to the thermodynamic stability of the complexes is the enthalpy term, dominated by formation of very strong σ-bonds between cyanide and thallium. These trends may prove useful for spectral/structural assignments but also for estimation of metal-to-ligand bond distances and stability constants for complexes which exist only in low concentration.

Introduction

Mixed-ligand complexes of metal ions have attracted attention since the 1950s.[1,2] Nevertheless, relatively little work has been done in this area, probably because of the complexity of ternary systems. During the last decade, the improvement of experimental methods and computer programs have made the evaluation of these complicated systems more facile.[3−5] Lately, the interest has increased due to the role of ternary compounds in natural multiligand systems, such as natural and polluted waters and body fluids. Due to its high relative NMR receptivity, ^{205}Tl has been used as a probe for studying metal ion functions in body fluids.[6] The thallium(I) ion, resembling the alkali cations, can be used to monitor a variety of biological activities, such as transmission of nerve impulses, distribution of water, regulation of metabolism, and activation and regulation of enzymes. The use of thallium(III) for similar purposes is not very common yet, but it has been applied in some important studies, such as the investigation of the human serum transferrin.[7] In the latter study, Fe(III) was replaced by Tl(III), whereupon the binding sites, the pH range for a Tl(III)−transferrin derivative, and the affinity for the C- and N-terminal sites in transferrin could be determined.

Thallium(III) in aqueous solution is known to be a strong oxidant. It is generally assumed that pseudohalide ions, with their reducing properties, cannot exist in solutions containing thallium(III), since they undergo immediate oxidation.[8] However, the existence of thallium(III) cyanide complexes has been reported, and these are established to be very strong and stable in acidic aqueous solution.[9] Thallium(III) chlorides and bromides have been investigated and known for decades, and much work has been done in this area.[10−19] Very recently, we determined the structures of the thallium(III) halide (Cl, Br) and thallium(III) cyanide complexes in aqueous solution.[20] We also studied ligand and electron exchange reactions of thallium(III) in aqueous solution.[21−27] For the Tl^{3+}−Cl^- and Tl^{3+}−

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Br^- systems we proposed an unusual ligand exchange mechanism where two positively charged complex ions, for example, Tl^{3+}(aq) and TlX^{2+}(aq), form an activated binuclear complex, $[(H_2O)_5Tl-X-Tl(OH_2)_5]^{5+}$.[22,23] A similar "complex-to-complex" exchange mechanism dominates also for the corresponding cyanide exchange reactions.[21,28] In order to gain a deeper understanding of this unusual reaction mechanism, we decided to investigate ligand exchange reactions in aqueous solutions containing ternary Tl(III)−CN−Cl complexes.[29] However, the latter complexes have not been reported in the literature. The present work aims at establishing the equilibria and compositions of the mixed thallium(III)−cyanide−halide complexes in aqueous solution using ^{205}Tl NMR spectroscopy and can also be seen as an attempt to understand the complex formation of the strongly oxidizing thallium(III) ion in aqueous solution. The study of Tl−CN−Br complexes had to be limited to only one ternary complex, namely $Tl(CN)Br^+$, due to the reduction of Tl(III) by Br^- in a large part of the suitable concentration range.

The soft thallium(III) ion binds strongly to the soft cyanide ligand, and four complexes with the composition $Tl(CN)_m{}^{3-m}$(aq) are formed.[9] In chloride solutions, thallium can coordinate up to six chloride ions.[31] The maximum number of ligands in the ternary complexes turned out to be 4, but the study of the system was still relatively complicated. Many of the 15 possible complexes, $Tl(CN)_mCl_n{}^{3-m-n}$ ($m + n \le 4$), never dominate, and some of them exist only as small fractions of the total thallium concentration. In order to be able to observe all the existing complexes, ^{205}Tl NMR spectroscopy with its high sensitivity and resolution was employed. Currently, NMR spectroscopy can be used effectively to solve equilibrium chemistry problems, and its role within this field of chemistry is increasing rapidly.[32] Linear correlations between the NMR parameters and the physical properties of the investigated species can sometimes be extracted from such data,[33−35] yielding additional structural information. This is also the case in the present study, in which the obtained ^{205}Tl NMR individual chemical shifts and ^{205}Tl−^{13}C spin−spin coupling constants have been related to chemical/physical properties of the studied complexes.

Experimental Section

Materials and Analysis. All solutions were prepared from a concentrated stock solution of $Tl(ClO_4)_3$ ($[Tl^{3+}] = 1.45$ M in 3.77 M $HClO_4$), which was prepared by anodic oxidation of $TlClO_4$ as described previously.[36,37] Solutions with suitable $Tl^{3+}/CN^-/Cl^-$ ratios for the ^{205}Tl NMR measurements were prepared in the following way. The total Tl(III) concentration was kept constant at 50 mM, whereas the concentrations of chloride (bromide) and cyanide were varied between 0 and 300 mM, by addition of solid LiCl (NaBr) and NaCN to the solutions. The acid content for solutions with low CN/Tl ratios was kept between 1 and 2 M to prevent hydrolysis of thallium(III). The ionic medium in all solutions was ($LiClO_4 + HClO_4$) = 3 M. In order to obtain more accurate values of the ^{205}Tl−^{13}C spin−spin coupling constants, some solutions were ^{13}CN-enriched (>99%) by adding solid $Na^{13}CN$ (Merck, analytical grade).

The concentrations of H^+, Tl^+, and Tl^{3+} in the studied solutions were analyzed as described previously.[19,38,39]

NMR Measurements. ^{205}Tl NMR spectra were recorded at a probe temperature of 298 (±0.5) K with a Bruker MSL90 (at 51.9 MHz) and a Bruker AM400 (at 230.8 MHz) spectrometer. The MSL90 spectrometer was preferred for quantitative measurements, since the smaller spectral windows and shorter 90° pulses gave more quantitative spectra. Whenever a better resolution or sensitivity was desired, the spectra were recorded on the AM400 spectrometer. Moreover, due to complicated ligand exchange phenomena, it was of importance to record spectra at two magnetic fields. The NMR parameters were chosen so that quantitative spectra were obtained; typically (MSL 90), the pulse width was 3 μs (≈30°), the pulse repetition time 1.0 s, spectral window 70 kHz, and the number of scans 10 000−100 000. The T_1 values were typically in the range 0.1−0.5 s; the longest one was 2.0 s for the $Tl(OH_2)_6{}^{3+}$ ion. The chemical shifts are accurate within ±0.2 ppm and are reported in ppm toward higher frequency with respect to an external aqueous solution of $TlClO_4$ extrapolated to infinite dilution at 298 K. Since the chemical shifts for aqueous solutions of different Tl(I) salts extrapolate to the same value of infinite dilution,[40] this value corresponds to the chemical shift of the free hydrated Tl^+ ion.

Results and Calculations

NMR Spectra. All 15 possible complexes with the general formula $Tl(CN)_mCl_n{}^{3-m-n}$ ($m + n \le 4$) have been identified using ^{205}Tl NMR (Figure 1). The concentrations of the different thallium complexes and of the free ligands were varied during this study (*cf.* Figure 2) leading to notable alteration of the rates of ligand exchange.[22,23,28,41] At some solution compositions, pure cyanide complexes ($n = 0$) and complexes where $(m + n) \le 2$ exchange slowly on the actual ^{205}Tl NMR chemical shift and $^1J(^{205}Tl-^{13}C)$ time scales, thus giving rise to separate ^{205}Tl NMR peaks (Figure 1). The shifts and the spin−spin coupling constants of these sites were determined directly from the recorded ^{205}Tl NMR spectra. For higher complexes, $(m + n) \ge 3$, the chloride exchange is fast while the cyanide exchange remains slow. Hence, a single, population-averaged signal is observed for the complexes with a certain number of cyanide ligands, m, and varying number of chlorides, n, and the observed chemical shift depends on the average number of chlorides bound to thallium according to

$$\delta^m_{\mathrm{obs}} = \sum_n p_n \delta_{\mathrm{Tl(CN)}_m\mathrm{Cl}_n} \qquad (1)$$

where p_n is the thallium mole fraction and $\delta_{\mathrm{Tl(CN)}_m\mathrm{Cl}_n}$ the individual chemical shift of the $Tl(CN)_mCl_n{}^{3-m-n}$ complex. Using the computer program package LAKE,[42,43] we were able to determine the individual chemical shifts and spin−spin

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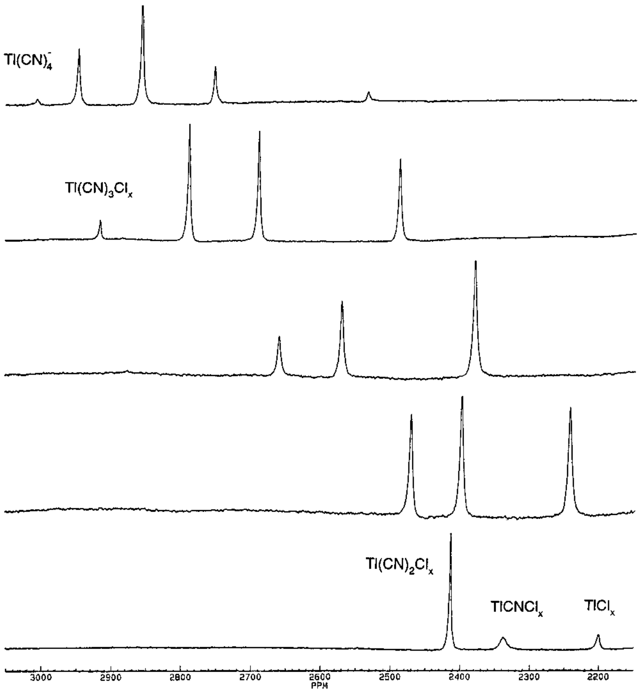

Figure 1. 51.9 MHz ^{205}Tl NMR spectra showing both fast and slow chemical exchange on the actual NMR chemical shift time scale for the Tl(CN)$_m$Cl$_n^{3-m-n}$ ($m + n \leq 4$) complexes.

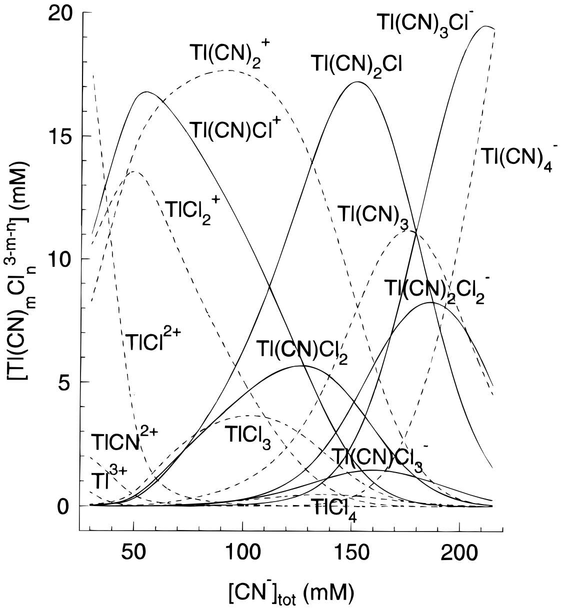

Figure 2. Distribution of Tl(CN)$_m$Cl$_n^{3-m-n}$ ($m + n \leq 4$) complexes as a function of the total cyanide concentration. The curves for the ternary Tl^{III}−CN$^-$−Cl$^-$ complexes are drawn with full lines, and those for the binary complexes, with dashed lines. [Tl^{III}]$_{tot}$ = [Cl$^-$]$_{tot}$ = 50 mM.

coupling constants, $^1J(^{205}\text{Tl}-^{13}\text{C})$, for the rapidly exchanging complexes. In cases of slow chloride exchange, direct determination of the spin−spin coupling constant was possible from the carbon-13 satellites. A ^{13}CN enrichment (≥99%) resulted in strong multiplets leading to a more accurate determination of the spin−spin coupling constants, ranging from about 5 to 15 kHz (Table 1). The line widths vary between 40 and 300 Hz due to relaxation of the nuclear spins and to the ligand exchange processes. The individual ^{205}Tl NMR chemical shifts and spin−spin coupling constants are given in Table 1.

Table 1. ^{205}Tl NMR Chemical Shifts,[a] Spin−Spin Coupling Constants, $^1J(^{205}\text{Tl}-^{13}\text{C})$, and Overall Formation Constants, β,[b] for Tl(CN)$_m$Cl$_n^{3-m-n}$ ($m + n \leq 4$) and Tl(CN)Br$^+$ Complexes in Aqueous Solution Containing Ionic Medium[c] at 25 °C (Estimated Standard Deviations in Parentheses)

complex	^{205}Tl shift, δ_{Tl} (ppm)	$^1J(^{205}\text{Tl}-^{13}\text{C})$ (kHz)	β
Tl^{3+}	2091[d]		
Tl(CN)$^{2+}$	2313[d]	14.73[d]	12.7(1)
Tl(CN)Cl$^+$	2338[d]	13.72[d]	19.1(1)
Tl(CN)Cl$_2$	2634(13)	10.58(9)	22.3(1)
Tl(CN)Cl$_3^-$	2759(10)	8.73(8)	24.6(1)
Tl(CN)$_2^+$	2415[d]	13.75[d]	25.5(2)
Tl(CN)$_2$Cl	2751(13)	10.61(8)	28.6(2)
Tl(CN)$_2$Cl$_2^-$	2865(10)	9.05(6)	30.9(2)
Tl(CN)$_3$	2847[d]	7.95[d]	34.0(3)
Tl(CN)$_3$Cl$^-$	2957(8)	6.91(3)	36.4(3)
Tl(CN)$_4^-$	3007[d]	5.44[d]	41.3(4)
TlCl^{2+}	2200[d]		7.13[e]
TlCl$_2^+$	2195[d]		12.55[e]
TlCl$_3$	2390(12)		16.00[e]
TlCl$_4^-$	2559(9)		18.40[e]
Tl(CN)Br$^+$ [f]	1762	12.42	

[a] The chemical shifts are given in ppm toward higher frequency with respect to an aqueous solution of TlClO$_4$ extrapolated to infinite dilution. [b] β = [Tl(CN)$_m$Cl$_n^{3-m-n}$]/{[Tl^{3+}][CN$^-$]^m[Cl$^-$]^n}. [c] 3 M {(H$^+$+Li$^+$),ClO$_4^-$}. [d] The NMR parameters of the slowly exchanging complexes, except for the hydrated Tl^{3+} ion, were kept constant in the LAKE calculations. [e] The formation constants for the binary thallium(III) chlorides, TlCl$_n^{3-n}$ (n = 1−4),[46] were used as constant parameters in the optimizations. [f] ^{13}C-enriched sample.

Determination of Stability Constants for Tl(CN)$_m$Cl$_n^{3-m-n}$ ($m + n \leq 4$). The formation of the ternary complexes was investigated by a gradual change of the Tl/CN/Cl ratio. The solutions were kept acidic, in order to prevent the formation of hydroxo complexes[36,44,45] and to avoid the precipitation of Tl$_2$O$_3$ (at pH >4). Hence, the following equilibria were studied:

$$\text{Tl(CN)}_m\text{Cl}_n^{\ 3-m-n} + \text{CN}^- \rightleftharpoons \text{Tl(CN)}_{m+1}\text{Cl}_n^{\ 2-m-n} \quad (m + n \leq 4) \quad (2)$$

Thus

$$K_{\text{CN}} = [\text{Tl(CN)}_{m+1}\text{Cl}_n^{\ 2-m-n}]/\{[\text{Tl(CN)}_m\text{Cl}_n^{\ 3-m-n}][\text{CN}^-]\} \quad (3)$$

and

$$\beta = [\text{Tl(CN)}_m\text{Cl}_n^{\ 3-m-n}]/\{[\text{Tl}^{3+}][\text{CN}^-]^m[\text{Cl}^-]^n \quad (m + n \leq 4) \quad (4)$$

^{205}Tl NMR spectra were recorded for the various solutions, and the peak integrals, chemical shifts, spin−spin coupling constants, $^1J(^{205}\text{Tl}-^{13}\text{C})$, and the analytical concentrations of the components were used for the determination of the overall formation constants, log β. The calculations were performed using the computer program LAKE, where the stability constants were least-squares-fitted to the NMR data for both the slow and the fast exchange regimes and the material balances for each solution.[42,43] In earlier measurements, the stability constants for the binary chloride complexes, TlCl$_n^{3-n}$ (n = 1−4), were determined in various ionic media.[10,11,13,19,46−49] The constants of Kul'ba,[46] valid for an ionic medium similar to the

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one of the present work,[50] were used and kept constant during the optimizations. Moreover, the experimentally measured coupling constants and chemical shifts for the *slowly exchanging* complexes (indicated in Table 1) were held constant during the optimizations. Also HCN was present in small concentrations in the studied solutions, and its pK_a value of 10.00 (in 3 M $LiClO_4$)[51] was included in the calculations. The four parameters for each complex, namely the coupling constant, the chemical shift, the signal integral, and the analytical concentration, have very different numerical values (see Supporting Information) and experimental accuracy. Thus, these parameters were weighted differently in order to obtain statistically relevant results with low residuals. The resulting stability constants and their corresponding standard deviations are given in Table 1.

Discussion

Stability Constants. Stepwise stability constants of MX_n complexes often decrease with increasing *n* because of statistical, steric, and Coulombic factors;[52] this is also the case for thallium(III) complexes with halides. The situation is somewhat different for the soft cyanide ligand, since it forms much stronger complexes with Tl(III) than do the halides (*cf.* Table 1 and ref 53), and the observed trend of the stepwise stability constants is $K_1 \approx K_2 > K_3 > K_4$. The equilibrium constant for the formation of the first cyano complex, $Tl(CN)^{2+}$, is large, log $K_1 = 12.7$, as is the second stepwise constant, log $K_2 = 12.8$. Also the addition of CN^- to $TlCl^{2+}$, yielding the $Tl(CN)Cl^+$ complex, is thermodynamically favored, log $K_{CN} = 12.0$. The same situation occurs for $Tl(CN)Br^+$; log $K_{CN} = 12.1$. The key to the explanation of this trend may lie in the structure of the formed species. The four complexes, $Tl(CN)^{2+}$, $Tl(CN)_2^+$, $Tl(CN)Cl^+$, and $Tl(CN)Br^+$, all with stepwise formation constants of about log $K = 12$, have probably a pseudooctahedral geometry with *trans*-X_1−Tl−X_2 units ($X_{1,2} = CN^-, Cl^-, Br^-, H_2O$).[20] The pronounced covalent character of the thallium−carbon bond leads to a decreased effective charge on thallium, whereupon the hydration becomes weaker. This reasoning is supported by the fact that the $Tl(CN)_2(OH_2)_4^+$ complex in water has about 0.1 Å longer Tl−O distances than the corresponding chloride or bromide complexes.[20] Hence, the main contributions to the equilibrium constant, namely the enthalpy and the entropy terms, are approximately unchanged among these four complexes, and this can be the reason for the similar thermodynamic stability of these complexes.

It is certainly not a coincidence that also diorganothallium(III) compounds containing the linear C−Tl−C group are extremely stable;[8,54] for example, the $Tl(CH_3)_2^+$ ion is stable in aqueous solution.[55] The significant strength of this type of linear or almost linear metal ion complex was previously observed for the cyanide complexes of the d^{10} ions copper(I), silver(I), probably gold(I), and mercury(II). There is some evidence that back-donation plays a role in cyano complexes. For the isoelectronic Au(I), Hg(II), and Tl(III) ions, the back-donation should be most efficient for gold and least efficient for thallium because of the increasing charge on the metal ion. Thus, if back-donation is an important effect, the stability constants for the cyano complexes should decrease in the order Au > Hg > Tl. Unfortunately, only one stability constant, namely β_2, is known for gold(I), but there is no doubt that the β_2 values follow the predicted trend log $\beta_2 = 39$ (for Au) > 32.7 (for Hg) > 25.5 (for Tl).[9,56,57] The same trend can be found for the logarithms of the stability constants for the monocyano complexes of Hg(II) and Tl(III), 17.0 and 12.7, respectively. However, in the tricyano and tetracyano complexes of Hg(II) and Tl(III), the opposite trend is found. This might indicate that in the last two complexes back-donation is less important compared to other factors, *e.g.* the higher positive charge of the thallium ion. On the other hand, these observations may also be ascribed to $5d_{z^2}$–6s mixing, which is more efficient for Hg(II) than for Tl(III) as discussed by Orgel[58] and Nyholm.[59] In fact, as will be discussed later, the role of back-bonding in the $Tl(CN)_mCl_n^{3-m-n}$ complexes is probably small in comparison to the σ-bond contribution.

When one cyanide is added to the complexes $TlCl_2^+$ and $Tl(CN)Cl^+$, the stepwise stability constants decrease by 2.5−3 logarithmic units (log $K_{CN} = 9.74$ and 9.55, respectively). The reason for this might be the change from the stable *trans*-octahedral to tetrahedral or trigonal-bipyramidal geometry.[20] The formation constants for addition of one cyanide ligand to the complexes $TlCl_3$, $Tl(CN)Cl_2$, and $Tl(CN)_2Cl$ are 8.65, 8.58, and 7.76, respectively. In these equilibria, the geometry does not necessarily change, but the constants decrease further by 1−2 units. This decrease might be due to the disadvantage of adding another electron-donating ligand to the metal center, whose positive formal charge is already relatively low.

Due to the softness of the Tl^{3+} ion, its ability to form strong complexes is more pronounced with cyanide than with chloride, as manifested by the larger stability constants for the former than for the latter complexes. An important difference though is that thallium(III) binds up to six chlorides[19,31] but only up to four cyanides.[9] A possible explanation may again be the formal positive charge of thallium(III), which is diminished more efficiently by the soft cyanide ligand than by the harder and smaller chloride. A similar situation occurs in the ternary cyano−chloro complexes where thallium does not accept more than four ligands.

Studies of complicated ionic equilibria are usually performed in solutions containing constant ionic media achieved by use of a supporting electrolyte with a concentration by far exceeding the concentration of the reagent species. With this methodology, the activity coefficients of the investigated species remain approximately constant. The stability constants, log β, for binary Tl(III) cyanide complexes were determined previously in 4 M [$NaClO_4 + LiClO_4 + HClO_4$] ionic medium.[9] In the present work, a 3 M ionic medium was used instead [($LiClO_4 + HClO_4$) = 3 M]. Certainly, the H^+ concentration could not be kept constant in the present study, but a replacement of Li^+ by H^+ does not change the specific interaction coefficients.[50,60] From these two sets of stability constants the interaction coefficients (ϵ) for the $Tl(CN)_m^{3-m}$ complexes were calculated in the same way as described previously[50,61] and are as follows

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(1σ in parentheses): $\epsilon[\mathrm{Tl(CN)^{2+},ClO_4^-}] = 0.33(12)$, $\epsilon[\mathrm{Tl(CN)_2^+,ClO_4^-}] = 0.03(18)$, $\epsilon[\mathrm{Tl(CN)_3}] = 0.01(21)$, $\epsilon[\mathrm{Tl(CN)_4^-,Na^+}] = -0.01(32)$, $\epsilon[\mathrm{Tl(CN)_4^-,Li^+}] = 0.08(33)$. Unfortunately, the standard deviations in the calculated ϵ values are high, depending on the standard deviations of the stability constants and because of the small differences between the two sets of the stepwise equilibrium constants (13.21, 13.29, 8.67, 7.44 and 12.7, 12.8, 8.5, 7.3, respectively). Thus, only the ϵ value for the monocyano complex is significantly different from zero. These values could then be used for calculation of the stability constants at other ionic strengths. The log K_m values for zero ionic strength were calculated to be 12.3, 11.9, 8.3, and 6.8, for $m = 1$, 2, 3, and 4, respectively (in this calculation, the ϵ values for $m = 2$, 3, and 4 were set to zero).

When two or more complex-forming ligands are present in solution, there is a possibility that ternary complexes are formed, as in this study. The stability of ternary complexes can be predicted from stability constants of binary complexes according to the following equation, given, *e.g.*, by Stumm and Morgan[62]

$$\log \beta_{\mathrm{MA}_m\mathrm{B}_n} = \frac{m}{m+n} \log \beta_{\mathrm{MA}_{m+n}} + \frac{n}{m+n} \log \beta_{\mathrm{MB}_{m+n}} + \log S \tag{5}$$

where S is the statistical factor expressing the number of ways in which these species can be formed:

$$S = \frac{(m+n)!}{m!n!} \tag{6}$$

For example, the stability of the complex $\mathrm{MAB^+}$ can be obtained from the known stability constants of the binary complexes $\mathrm{MA_2^+}$ and $\mathrm{MB_2^+}$:

$$\mathrm{M^{3+} + 2A^- \rightarrow MA_2^+(aq)} \qquad \beta(\mathrm{MA_2^+}) \tag{7}$$

$$\mathrm{M^{3+} + 2B^- \rightarrow MB_2^+(aq)} \qquad \beta(\mathrm{MB_2^+}) \tag{8}$$

$$\mathrm{M^{3+} + A^- + B^- \rightarrow MAB^+(aq)} \qquad \beta(\mathrm{MAB^+}) \tag{9}$$

$$\log \beta(\mathrm{MAB^+}) = [\log \beta(\mathrm{MA_2^+}) + \log \beta(\mathrm{MB_2^+})]/2 + \log A \tag{10}$$

log A is a parameter which depends on the effects of the statistical factor (a), electrostatic effect (b), coordination (or steric) effect (c), co-operative effect of ligands (d), and asymmetry of the ternary complex (e).[62,63] If the ligands are structurally equivalent, the importance of b−e is negligible compared to the statistical factor a and log A can be approximated by log S, which accounts solely for the statistical factor.

It was shown previously for various complexes of metal ions that such an estimation yields stability constants in good agreement with the experimental ones.[1,62,63] Also in the present case, the estimated stability constants for the $\mathrm{Tl(CN)}_m\mathrm{Cl}_n^{3-m-n}$ complexes using eq 5 are in accordance with the experimental values calculated using the LAKE software (Table 2). A comparison has been made with and without the statistical factor, and it is clear that the agreement between the estimated and experimental values is better with the statistical factor than without it. The difference between the estimated and experimental values ($\Delta \log \beta$) is not significant considering the standard deviations in β (see Table 1), and it can be concluded that the importance of b−e is negligible compared to a, though the ligands are not wholly structurally equivalent.

Table 2. Comparison between Overall Stability Constants, log β, Estimated Using Eq 5, and Experimental Overall Stability Constants, $\beta = [\mathrm{Tl(CN)}_m\mathrm{Cl}_n^{3-m-n}]/\{[\mathrm{Tl^{3+}}][\mathrm{CN^-}]^m[\mathrm{Cl^-}]^n\}$, Calculated with the LAKE Program[42,43]

complex	log β (eq 5)	log β (LAKE)	Δ log β
$\mathrm{Tl(CN)Cl^+}$	19.32 (19.02)[a]	19.09	0.23 (0.07)[b]
$\mathrm{Tl(CN)Cl_2}$	22.49 (22.01)	22.29	0.20 (0.28)
$\mathrm{Tl(CN)Cl_3^-}$	24.73 (24.13)	24.65	0.08 (0.52)
$\mathrm{Tl(CN)_2Cl}$	28.50 (28.02)	28.64	0.14 (0.62)
$\mathrm{Tl(CN)_2Cl_2^-}$	30.64 (29.87)	30.87	0.23 (1.00)
$\mathrm{Tl(CN)_3Cl^-}$	36.20 (35.60)	36.40	0.20 (0.80)
$\mathrm{Tl(CN)Br^+}$	21.4[c]		
$\mathrm{Tl(edta)CN^{2-}}$		8.72[d]	

[a] The values given in parentheses are calculated log β *without* the statistical factor S. [b] The values given in parentheses are the differences (Δ) between log β (eq 5) *without* S and log β [LAKE]. [c] log $K_{\mathrm{CN}} = 12.1$ (for $\mathrm{TlBr^{2+}}$, log $K = 9.28$[14]). [d] $K_{\mathrm{CN}} = [\mathrm{Tl(edta)(CN)^{2-}}]/\{[\mathrm{Tl(edta)^-}][\mathrm{CN^-}]\}$; from ref 24.

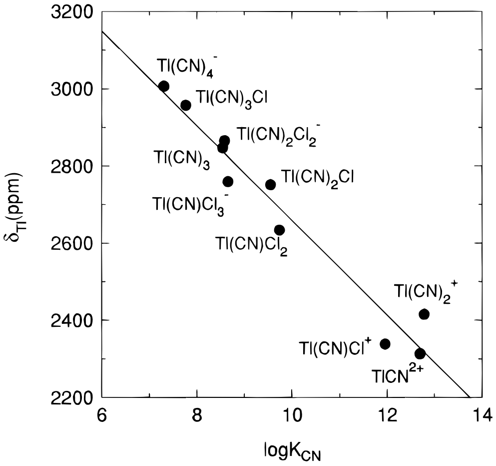

Figure 3. Individual ^{205}Tl NMR chemical shifts for the $\mathrm{Tl(CN)}_m\mathrm{Cl}_n^{3-m-n}$ ($m + n \leq 4$) complexes at 298 K as a function of their stepwise stability constants, log K_{CN}.

The overall stability constant (log β) for $\mathrm{Tl(CN)Br^+}$ was estimated according to eq 10 with the binary complexes $\mathrm{Tl(CN)_2^+}$ and $\mathrm{TlBr_2^+}$ as references (Table 2). The log β values used in the calculations were 16.7 for $\mathrm{TlBr_2^+}$ in 3 M $\mathrm{LiClO_4}$[14] and 25.5 for $\mathrm{Tl(CN)_2^+}$ (this work).

Chemical Shifts. The individual chemical shifts, δ_{Tl}, for the different $\mathrm{Tl(CN)}_m\mathrm{Cl}_n^{3-m-n}$ complexes were found to be linearly dependent on the stepwise equilibrium constants, log K_{CN} (Figure 3). Similar dependence has been reported previously by Öhrström *et al.* for the ^{103}Rh NMR shifts of the various $\mathrm{Rh^I}$(acetylacetonate)(alkene)$_2$ complexes[64a] and by Read *et al.* for the overall formation constants (β_6) of chloro and bromo complexes of Rh(III).[65] Also ^{59}Co NMR shifts for various cobalt(III) species were found to decrease linearly with increasing log β_6.[65] In all these cases, the relation was observed for a series of complexes with the same symmetry (square-planar or octahedral) and was discussed in terms of the paramagnetic term of the Ramsey equation (see below).[64b] Also in the present case, the ^{205}Tl NMR chemical shifts decrease linearly when the

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stability constants, log K_{CN}, become larger, but there are some important differences:

(1) The relation includes complexes with varying geometry, *e.g.* $Tl(CN)(OH_2)_5^{2+}$ (pseudooctahedral) and $Tl(CN)_4^-$ (tetrahedral).[20]

(2) The main contribution to the stepwise stability constants is probably the formation of the Tl−CN bond (*cf.* discussion in next section). The entropy contribution for the formation of the various complexes is apparently negligible since different numbers of water molecules are replaced by a cyanide. For example, the formation of $Tl(CN)(OH_2)_5^{2+}$ from $Tl(OH_2)_6^{3+}$ releases one water molecule (and probably increases the Tl−OH_2 distances to the remaining ones), whereas the formation of $Tl(CN)_3(OH_2)$ from $Tl(CN)_2(OH_2)_4^+$ releases three water ligands.[20] In fact, this assumption finds some support in the thermodynamic data for the isoelectronic $Hg(CN)_n^{2-n}$ complexes ($n = 1, 2$) where the enthalpy contribution to $\Delta G°$ is of major importance: $\Delta H_1° = -96$, $T\Delta S_1° = 0.8$ and $\Delta H_2° = -107$, $T\Delta S_2° = 17$ kJ/mol.[66]

The Ramsey equation describes the chemical shift for the atom A (δ_A) as composed of two terms, diamagnetic (δ_{dia}) and paramagnetic (δ_{para}),[67] where δ_{dia} involves the free rotation of electrons about the nucleus in question and δ_{para} describes the hindrance of this rotation caused by other electrons and nuclei in the molecule. There have been several attempts to calculate chemical shifts, but there are some problems difficult to overcome.[68,69] The main obstacle is the large size of both contributions, δ_{dia} and δ_{para}, and their opposite signs, which means that the chemical shift becomes a small difference between two large and variable terms leading to a relatively large error. For heavy atoms, the additional difficulty of calculating the large relativistic correction makes the task even more intricate.[70−72] Therefore, we confine ourselves to a qualitative discussion of the observed trends of ^{205}Tl NMR chemical shifts. For this purpose, a simplified form of the Ramsey equation can be written:[73,74]

$$\delta_A = \delta_{dia} + \frac{K\langle r^{-3}\rangle}{\Delta E}\sum_B Q_{AB} \qquad (11)$$

where K is a constant, $\langle r^{-3}\rangle$ is the mean radial factor of the valence orbitals, ΔE is the mean excitation energy, and $\sum_B Q_{AB}$ is the charge density term where the summation includes all atoms in the molecule (also A). The diamagnetic contribution (δ_{dia}) is mainly due to the core electrons and can determine the chemical shifts of the lightest nuclei, but *e.g.*, for the heavier rhodium it has been shown that in ^{103}Rh NMR δ_{dia} is not significantly different for Rh^I and Rh^{III} compounds.[64,65] Hence, for the ^{205}Tl NMR chemical shifts of the various thallium species δ_{dia} can safely be assumed to remain constant and the paramagnetic term originating from the chemical environment of thallium will determine the chemical shifts (*cf.* Table 1 and Figure 3).

The previous discussion of the paramagnetic term of the Ramsey equation has concerned the chemical shifts of transition metal complexes,[64,65,74−77] and it has been concluded that trends of δ_{para} can be rationalized using the ligand field theory. The mean excitation energy, ΔE, is usually approximated by the lowest energy optical transition. Unfortunately, the optical spectral parameters of the $Tl(CN)_mCl_n^{3-m-n}$ complexes have not been reported, and even if the electronic spectra would be recorded, they would demand careful mathematical treatment since usually a number of complexes are present in solution (Figure 2). In order to estimate the trends of ΔE for different complexes of d transition metal ions, the spectrochemical series is normally applied. Also for thallium(III) compounds, orbital mixing involving 5d electrons has been envisaged.[58,59] If we use the predictions of the spectrochemical series also in the present case, the cyanide ligand would be expected to lead to a larger ΔE term than does H_2O, thus lowering the ^{205}Tl NMR chemical shifts when a water ligand on Tl(III) is replaced by a cyanide (eq 2). However, the opposite trend is observed (Figure 3), and we conclude that ΔE is not a major term determining the chemical shifts.

Of the two remaining factors in eq 11, the radial term $\langle r^{-3}\rangle$ may result from the delocalization of the valence electrons of the metal, resulting in a weaker interelectronic repulsion. This would be proportional to the covalent character of the metal−ligand bonds and would depend on the position of the ligand in the nephelauxetic series.[78] The cyanide ligand would thus lead to smaller $\langle r^{-3}\rangle$ compared to H_2O, which would decrease the ^{205}Tl NMR chemical shift. Again, the experimental values show the opposite trend. Hence, if the applied assumptions are correct, we have no other choice than to consider the charge density term as the major contributor to the chemical shift changes shown in Figure 3. In connection with the assumption made above (*cf.* point 2 earlier in this section), the linear correlation of Figure 3 indicates that the electron donation from the cyanide ligand to the metal ion plays the most important role. This conclusion is in agreement with the experimental information obtained from the spin−spin coupling constant correlations (*cf.* discussion in next section). In its extreme form, the charge density term has a major influence on the chemical shifts of many heavy elements in varying oxidation states. For example, ^{129}Xe NMR shifts vary from −5331 ppm for Xe^0, through −1750 ppm for $Xe^{II}F_2$, +253 ppm for $Xe^{IV}F_4$, 0 ppm for $Xe^{VI}OF_4$, to +2077 ppm for $Xe^{VIII}O_6^{4-}$.[79] Thallium-205 NMR shifts of thallium(I) compounds are typically in the range −200 to +200 ppm, whereas the corresponding range for thallium(III) compounds is +2000 to +3000 ppm.[6,53,80]

A replacement of a chloride ligand by a cyanide, *e.g.* between $Tl(CN)Cl^+$ and $Tl(CN)_2^+$ or between $TlCl_3$ and $Tl(CN)Cl_2$, does not have a similar linear effect. A substitution of water molecule(s) by chloride or bromide does not lead to a linear plot similar to that in Figure 3 but rather mirrors changes in the geometry of the complexes.[19,20] Possibly, the effects of the breaking of the Tl(III)−chloride bond is not negligible compared to the Tl−CN bond formation. On the other hand, the Tl(III)−

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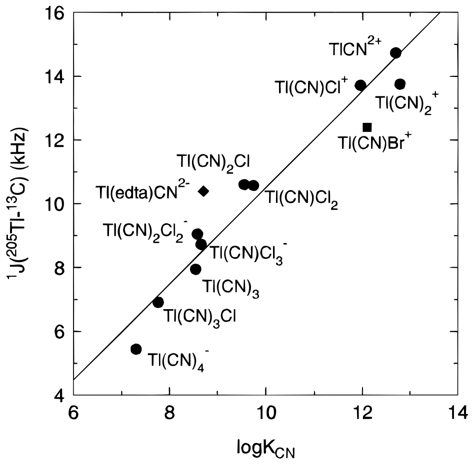

Figure 4. Correlation between the spin−spin coupling constants, $^1J(^{205}\mathrm{Tl}-^{13}\mathrm{C})$, for the $\mathrm{Tl(CN)}_m\mathrm{Cl}_n{}^{3-m-n}$ ($m + n \leq 4$), $\mathrm{Tl(edta)CN}^{2-}$, and $\mathrm{Tl(CN)Br}^+$ complexes and their stepwise stability constants, log K_{CN}.

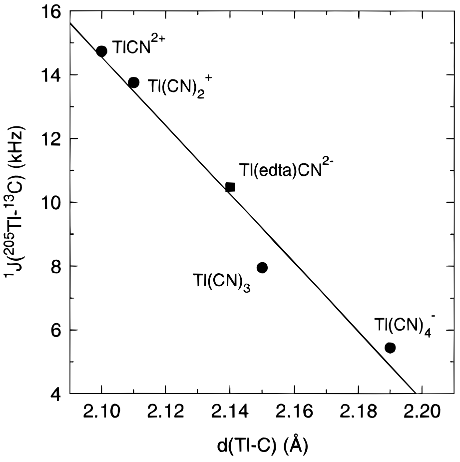

Figure 5. Correlation between the spin−spin coupling constants, $^1J(^{205}\mathrm{Tl}-^{13}\mathrm{C})$, for the complexes $\mathrm{Tl(CN)}_m{}^{3-m}$ and $\mathrm{Tl(edta)CN}^{2-}$ ($m \leq 4$) and the internuclear distance, $d_{\mathrm{Tl-C}}$.[20] (Note that the Tl−C distance in $\mathrm{Tl(CN)}^{2+}$ is an estimated value.)

halide bond is not so much stronger than the Tl(III)−water bond that the breaking of the latter can be neglected.

Spin−Spin Coupling Constants. The large coupling constants, $^1J(^{205}\mathrm{Tl}-^{13}\mathrm{C})$, confirm the existence of the strong Tl−C bonds with a pronounced s character in thallium(III)−cyano−chloro complexes. For example, the complexes $[\mathrm{Cl-Tl-CN}]^+$ and $[\mathrm{CN-Tl-CN}]^+$ have several times larger spin−spin coupling constants than the organometallic $[\mathrm{H_3C-Tl-CH_3}]^{3+}$ entity, where $^1J(^{205}\mathrm{Tl}-^{13}\mathrm{C})$ varies from 2100 to 5800 Hz, and the coupling constant for the $\mathrm{Tl(CN)_3}$ complex is 4−5 times larger than that for the trimethylthallium compounds (which is less than 2000 Hz).[80−82]

The spin−spin coupling constants show a nearly linear dependence on the stepwise equilibrium constants (Figure 4). This is somewhat surprising since spin−spin coupling between two nuclei is a direct measure of the bond strength, s-electron participation in bonding orbitals (through the Fermi contact term), and induced currents in the molecular electron cloud but has apparently no connection to the equilibrium constant for the association of a new ligand. The explanation is provided by the observed correlation between the coupling constants and the Tl−CN force constants[20] (see Supporting Information). For a series of molecules of the same type, there is a relation between the force constant and the bond strength, expressed as the dissociation energy of the bond.[83] Thus, the force constant reflects the strength of the Tl−CN bond.[84] Concluding, of all contributions to the Gibbs' free energy of formation of a complex, the enthalpy term, reflecting the strength of the Tl−CN bond, is the dominating one. This indicates also that the s characters of this bond in the different $\mathrm{Tl(CN)}_m\mathrm{Cl}_n{}^{3-m-n}$ complexes are very similar. Indeed, in a recent study[85] it was concluded that the metal−carbon bond in, *e.g.*, $\mathrm{Tl(CN)_2}^+$ and $\mathrm{Hg(CN)_2}$ has to a large extent covalent character, where σ-bonding dominates over the $d \rightarrow \pi^*$ back-bonding. The calculated contribution from the back-bonding was only 3.6% of the total covalent bonding in the $\mathrm{Tl(CN)_2}^+$ complex. Thus, assuming that these bonding properties are approximately the same in the other $\mathrm{Tl(CN)}_m\mathrm{Cl}_n{}^{3-m-n}$ complexes, the non-s-character contributions can be neglected and only the Tl−CN bond strength would determine the spin−spin coupling constant, giving rise to the obtained linearity in Figure 4. This explains also the linear relationship observed between the spin−spin coupling constant and the internuclear distance, $d_{\mathrm{Tl-C}}$ (Figure 5), since this distance is a direct measure of the strength of the Tl−CN bond.

A similar dependence of the metal−ligand nuclear spin−spin coupling on the metal−ligand distance was observed by Heaton *et al.*, who investigated different rhodium carbonyl clusters.[33] Despite the presence of other ligands on rhodium, $^1J(^{103}\mathrm{Rh}-^{13}\mathrm{CO})$ was in most cases linearly dependent on the Rh−C bond length. The same group have reported another correlation of this type for diverse carbonyl sites in $[\mathrm{NiRh_6(CO)_{16}}]^{2-}$. The resulting plot was not completely linear but had a smooth increase in ^1J with decreasing metal−carbon distance.[34] Very recently, they investigated rhodium(I) phosphine complexes, $[\mathrm{RhX(PPh)_3}]$ (where X = Cl, $\mathrm{ONO_2}$, $\mathrm{CH_3CN}$, $\mathrm{NH_3}$), and found a linear relationship between $^1J(^{103}\mathrm{Rh}-^{31}\mathrm{P})$ and $d_{\mathrm{Rh-P}}$.[35] The underlying reasons behind these relationships were not discussed in these papers, but the plots were used for structural and spectral assignments.

Two other trends for the Tl−C spin−spin coupling constants can be noted: $\mathrm{Tl(CN)}^{2+} > \mathrm{Tl(CN)Cl}^+ > \mathrm{Tl(CN)Cl_2} > \mathrm{Tl(CN)Cl_3}^-$ and $\mathrm{Tl(CN)_2}^+ > \mathrm{Tl(CN)_2Cl} > \mathrm{Tl(CN)_2Cl_2}^-$. Here, the influence of an added ligand on the Tl−C bond is more difficult to evaluate, since the increase of the coordination number changes also other factors, such as geometry, entropy, and charge on the metal ion. Still, it can be concluded that, for every new ligand, the Tl−C bond is weakened, which might be due to an increased saturation of the positive charge on thallium.[86]

Mixed cyano complex formation with halides has previously been observed for the isoelectronic mercury(II) and for the cadmium(II) ion.[87,88] The maximum coordination number for the mercury complexes is also 4, and the formation constants exhibit a behavior similar to those of the binary metal cyanide systems, namely that Hg(II) forms stronger bonds than Tl(III)

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(81) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: London, 1978; p 302.

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(84) Principally, it is difficult to formulate a general theoretical relation between the force constant and the dissociation energy. The force constant is a measure of the curvature of the potential well near the equilibrium position, whereas the dissociation energy is given by the depth of the potential energy curve. Thus, a large force constant means a sharp curvature of the potential well near the bottom but does not necesserily imply a deep potential well. However, for a series of molecules of the same type, a large force constant usually indicates a strong bond.

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with the first two cyanide ligands, whereas this order is reversed for the third and fourth cyanide complexes.

Other Ternary Thallium(III) Cyanide Complexes. Recently, the mixed ligand complex $Tl(edta)CN^{2-}$ was established and studied.[24] The thallium ion in this complex is hexacoordinated by an "edta-basket" and has a total coordination number of 7. Another mixed thallium(III) cyanide complex, $Tl(CN)Br^{+}$, is presented for the first time in this paper. Some experiments were made on the $Tl(III)-CN^{-}-Br^{-}$ system, but due to the reduction of Tl(III) by bromide, the system was not further investigated. The reduction of Tl(III) in the binary $Tl(III)-Br^{-}$ system can be prevented by an addition of Br_2, but this method could not be used in the present case since Br_2 oxidized the cyanide. From ^{13}C NMR, the coupling constant for $Tl(CN)Br^{+}$ was found to be 12.42 kHz.

The addition of cyanide to $Tl(edta)H_2O^{-}$ conforms neither to the linear dependence between the chemical shift and stability constant in Figure 3 ($\delta_{Tl} = 2460$ ppm, $\log K_{CN} = 8.72$[24]) nor to the $^{1}J(^{205}Tl-^{13}C)$ *vs* $\log K_{CN}$ dependence of Figure 4. This is certainly caused by the different coordination of the thallium atom in $Tl(edta)CN^{2-}$ as compared to the $Tl(CN)_mCl_n^{3-m-n}$ species, since this influences the value of $\log K$. The latter is dependent not only on the Tl−C bond strength but also on the type of coordination. However, the data for $Tl(edta)CN^{2-}$ fall on the straight line of Figure 5, apparently because the Tl−C distance is a true measure for the Tl−CN bond strength.

The $Tl(CN)Br^{+}$ complex is probably structurally similar to $Tl(CN)Cl^{+}$, and it falls close to the straight line of Figure 4. However, this is not the case in Figure 3 possibly because of the so-called "heavy-atom effect"[89] which causes δ_{Tl} to fall to a much lower value (1762 ppm; $\log K_{CN} = 12.1$). The overall stability constant for $Tl(CN)Br^{+}$ estimated from the binary $TlBr_2^{+}$ and $Tl(CN)_2^{+}$ complexes using eq 5,[62,63,90,91] (Table 2) shows that, compared with chloride, the bromide ligand supplies additional stability to the mixed thallium cyanide complex.

Concluding Remarks

The study of the ternary system $Tl(III)-CN^{-}-Cl^{-}$ in acidic aqueous solution turned out to be quite intricate, with nearly 20 species potentially present in solution (15 complexes $Tl(CN)_mCl_n^{3-m-n}$ ($m + n \leq 4$), $TlCl_5^{2-}$, $TlCl_6^{3-}$, HCN, CN^{-}). Several of these species exist only in very low concentration, and ^{205}Tl NMR spectroscopy (supported by ^{13}C NMR) has been shown to be particularly well suited for evaluation of the involved equilibria. An additional complication of the study was due to the occurrence of both slow and fast ligand exchange on the actual ^{205}Tl NMR chemical shift and $^{1}J(^{205}Tl-^{13}C)$ time scales. The elucidation of the chemical equilibria in this system would probably not be successful without the specially designed computer software LAKE,[42,43] which can handle multimethod equilibrium data with special emphasis on the different types of NMR information.

Acknowledgment. The authors are grateful for the continuous financial support from the Swedish Natural Science Research Council (NFR).

Supporting Information Available: A table giving analytical compositions, experimental ^{205}Tl NMR chemical shifts, peak integrals and $^{1}J(^{205}Tl-^{13}C)$ values for the studied solutions, a predominance diagram for $Tl(CN)_mCl_n^{3-m-n}$ complexes, correlation between $^{1}J(^{205}Tl-^{13}C)$ and the Tl−CN force constant (4 pages). Ordering information is given on any current masthead page.

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(86) A comparison can also be made between the spin−spin coupling constants for complexes with the same number but varying quality of ligands. Here, the changes in coordination geometry, and hence entropy changes, are probably relatively small and can be disregarded. The coupling constant trends for $^{1}J(^{205}Tl-^{13}C)$ are as follows: $Tl(CN)Cl_2 \approx Tl(CN)_2Cl \gg Tl(CN)_3$ and $Tl(CN)Cl_3^{-} \approx Tl(CN)_2Cl_2^{-} \gg Tl(CN)_3Cl^{-} \gg Tl(CN)_4^{-}$. In these trends, where the number of ligands is unchanged (3 and 4, respectively), the largest coupling constants occur for the complexes where the number of the cyano ligands is 1 or 2, possibly due to the extreme stability of the linear X_1-Tl-X_2 entity as discussed above.

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