state potential energy surface that, depending on the levels of electronic and vibronic coupling, can have four minima. The pyridine–pyridine intermolecular interactions (Figure 1) have been treated by the molecular field approximation. Furthermore, Stratt and Adachi[22] took the insightful approach of employing a "spin"-type Hamiltonian, which leads logically to the idea of two interpenetrating sublattices of M₃O complexes. Figure 10 shows the phase diagram for these complexes. J_1 and J_2 are parameters that gauge the pairwise intermolecular interaction where two neighboring M₃O complexes are distorted parallel to each other or only one is distorted, respectively. At low temperatures, phase I (ferrodistortive phase) exists where all M₃O complexes are valence trapped, and because of strain dipoles, the sense of distortion of each M₃O complex is the same. In phase II (antiferrodistortive phase), two interpenetrating sublattices exist where one sublattice has valence-trapped complexes and the sense of distortion (i.e., which ion is the M^{II} ion) is random. The other sublattice has an appreciable number of undistorted (delocalized) complexes mixed with randomly oriented localized complexes. In phase III (paradistortive phase), there is random distribution of distorted and undistorted complexes, where each M₃O complex is probably tunneling rapidly between its four vibronic states. Phase IV is described as having two sublattices as in phase II, but with both sublattices "ferromagnetic" and distorted in the same direction. It is important to note that only the phase boundary between I–III, I–II, and IV–II phases gives first-order transitions. The other lines correspond to second-order transitions.

The differences in behavior between the present Mn₃O complex and the isostructural Fe₃O complex can be rationalized in terms of the phase diagram given in Figure 10. Previously, we explained the presence of two phase transitions in [Fe₃O(O₂CCH₃)₆-(py)₃](py) by saying that the first-order phase transition at ~112

K occurred between phases I and II. This is immediately followed by the onset of a higher order phase transition at ~115 K, which culminates at ~190 K at the phase II–III line. Because the Mn₃O complex has somewhat different a, b, and c unit cell parameters than the Fe₃O complex, the pyridine–pyridine intermolecular interactions are likely of different magnitude. The Mn₃O complex could have a J_2/J_1 ratio such that the only phase transition occurring is the first-order one between phases I and III. The Mn₃O complex converts directly between the ferrodistortive phase and the paradistortive phase without ever becoming the antiferrodistortive phase. Variable-temperature neutron diffraction experiments are planned in an effort to obtain direct evidence for the presence of interpenetrating sublattices of Mn₃O complexes.

Regardless of the detailed description of the phase present in [Mn₃O(O₂CCH₃)₆(py)₃](py), it is amazing how cooperatively the valence detrapping occurs in this complex. There is long-range order as a result of appreciable intermolecular interactions. Not only are there appreciable intermolecular pyridine–pyridine interactions, but the interactions between Mn₃O complexes and pyridine solvate molecules are probably also important. It is clear that there is a sudden change from static to dynamic in the solvate structure at the 184.65 K phase transition. The two pyridine solvate molecules above and below each Mn₃O complex serve in essence as a small part of a solvate cage. The van der Waals interaction between a solvate molecule positioned asymmetrically relative to the C_3 axis of a nearby Mn₃O complex may lead to an intermolecular interaction energy of only 10–100 cm⁻¹ per solvate molecule. This amount of energy may modify the ground-state potential energy surface of the Mn₃O complex and consequently appreciably affect the rate at which such a complex can tunnel from one vibronic minimum to another.

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Determination of Stability Constants for Thallium(III) Cyanide Complexes in Aqueous Solution by Means of ¹³C and ²⁰⁵Tl NMR[1]

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Abstract: In contrast to what is usually assumed, we have found and proved that thallium(III) forms very strong cyanide complexes in aqueous solution. We have investigated this system using ²⁰⁵Tl, ¹³C, and ¹⁴N NMR and potentiometry and established the existence of four thallium(III)–cyanide complexes of the composition Tl(CN)$_n^{3-n}$, $n = 1$–4. We have measured their chemical shifts and spin–spin coupling constants and determined their formation constants at 25 °C in dilute (0.05 M) aqueous solution in the ionic medium ([Na⁺] = 1 M, [Li⁺] + [H⁺] = 3 M, [ClO₄⁻] = 4 M). The overall formation constants are log β_1 = 13.2 (1), log β_2 = 26.5 (2), log β_3 = 35.2 (2), and log β_4 = 42.6 (2). We have also determined the stability constant for HCN in the same ionic medium, log K_a = 10.11 (5). One-bond spin–spin coupling constants between thallium and carbon, ^1J(²⁰⁵Tl–¹³C), for the mono- and dicyano complexes of thallium(III) are 14636 and 13749 Hz, respectively, and appear to be the largest known coupling constants between these nuclei. The stability of the Tl(CN)$_n^{3-n}$ complexes is discussed in terms of their kinetic inertness.

The soft thallium(III) ion forms very strong complexes in solution. For example, its chloride and bromide complexes are among the strongest metal-ion halide complexes known. The soft cyanide ion, on the other hand, is a very important complexing ligand and forms strong complexes with most of the transition elements and the d¹⁰ ions. Also the Hg(II) ion, which is isoelectronic and has similar properties as Tl(III), forms very strong cyanide complexes.

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(1) Presented at the XIX International Conference on Solution Chemistry, Lund, Aug 1988. (cf. Abstracts, p 85).

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In textbooks and scientific literature, it is sometimes assumed that thallium(III) does *not* form cyanide complexes[2] (with the possible exception of $Tl(CN)_4^-$) or, often, this chemical system is not mentioned at all.[3a,4] The reason for thallium(III) not forming cyanide complexes is supposed to be its reduction according to the reaction

$$Tl^{3+} + 2CN^- \rightleftharpoons Tl^+ + (CN)_2(g) \qquad (1)$$
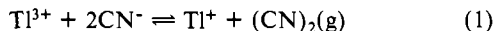
which is expected on the basis of the redox potentials. This is analogous to what happens in the $Tl(III)-I^-$ system: $Tl(III)$ is reduced to $Tl(I)$ (except for high I/Tl ratios where the species TlI_4^- has been found[5]). Moreover, Tl^{3+} normally exists only in strongly acidic solutions where the CN^- concentration is very low. There are nonetheless a few reports in the literature on the existence of thallium–cyanide complexes. In the solid state, the compound $Tl(CN)_2$ is assumed to have the composition Tl^I-$[Tl^{III}(CN)_4]$.[6a] Penna-Franca and Dodson[7] investigated the effect of cyanide on the thallous–thallic exchange reaction in aqueous solution, and to explain the results, they suggested the existence of the species $TlCN^{2+}$ and $Tl(CN)_2^+$ and thought it reasonable that $Tl(CN)_3$ and $Tl(CN)_4^-$ exist as well. Using their kinetic data, they also calculated $K_2/K_1 = 0.15$. Horne[8] estimated K_n, $n = 1$, 2 (?), to be less than 10^{11} and suggested the existence of $Tl(CN)_3$ and $Tl(CN)_4^-$ from cation-exchange resin adsorption data. Finally, a value of log $\beta_4 = 35$, estimated from the 84-year-old data of Spencer and Abegg,[9] can be found in ref 10.

In the present paper, we describe an investigation of the system $Tl(III)-CN^--H^+$ in aqueous solutions (containing the ionic medium $\{[Na^+] = 1\ M, [Li^+] + [H^+] = 3\ M, [ClO_4^-] = 4\ M\}$) using a multinuclear ($^{205}Tl$, ^{13}C, and ^{14}N) NMR technique and potentiometry. The total thallium concentration was kept at 0.05 M; the cyanide/metal ratio was varied between 0 and 6.3.

Experimental Section

Materials. A concentrated solution of $Tl(ClO_4)_3$ was obtained by anodic oxidation of $TlClO_4$.[11] From this solution, two stock solutions were prepared, one containing 50 mM Tl^{3+} in ionic medium (2 M $HClO_4$, 1 M $LiClO_4$, and 1 M $NaClO_4$) and the other containing 50 mM Tl^{3+}, ~120 mM $HClO_4$, and ~300 mM NaCN in ionic medium (3 M $LiClO_4$ and 1 M $NaClO_4$). These two stock solutions were then mixed to give solutions with various CN^-/Tl^{3+} ratios. For some of the NMR measurements, ^{13}CN-enriched solutions (≥99%) were used in order to increase the sensitivity of ^{13}C NMR measurements. For the compositions of the solutions, see Table I.

Analyses. The acid concentration of Tl(III) solutions was determined by titration with NaOH after adding an excess of solid NaCl to the analyzed solution. The concentration of Tl(I) was determined by titration with a calibrated 0.1 M solution of $KBrO_3$ using methyl orange as indicator. The total thallium content was obtained by reduction of Tl(III) with SO_2, boiling off the excess SO_2 and titrating with 0.1 M $KBrO_3$.[12] In this way, the concentrations of acid, Tl(I), and Tl(III) could be determined one after the other in the same sample.

pH Measurements. pH values were measured by means of a combination glass electrode (Radiometer GK2401B) in connection with a pH meter (Radiometer PHM62). The readings of the electrode were calibrated to pH values by using the method of Irving.[13] The ionic product of water in the present ionic medium was determined to be $pK_w = 13.98$ (± 0.05).

Figure 1. 230.8-MHz ^{205}Tl NMR spectra for different $[CN^-]_{tot}/[Tl^{3+}]_{tot}$ ratios. The numbers over the peaks denote n in $Tl(CN)_n^{3-n}$. The chemical shifts are given in ppm toward higher frequency with respect to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution.

Figure 2. 51.9-MHz ^{205}Tl NMR spectra for ^{13}C-enriched solutions for different $[CN^-]_{tot}/[Tl^{3+}]_{tot}$ ratios. The numbers over the peaks denote n in $Tl(CN)_n^{3-n}$. The chemical shifts are given in ppm toward higher frequency with respect to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution.

NMR Measurements. ^{205}Tl NMR spectra have been recorded at 51.9 MHz and at a probe temperature of 25 (± 0.5) °C with a Bruker MSL90 spectrometer. The NMR parameters were chosen so that quantitative spectra were obtained, typically flip angle ~45° (3 µs), pulse repetition time 1 s, spectral window ~70 kHz, number of scans 20000–85000. (Some ^{205}Tl NMR spectra have been recorded at 230.8 MHz with a Bruker AM400 spectrometer.) The chemical shifts are accurate within ± 0.02 ppm and are reported in ppm toward higher frequency with respect to an external aqueous solution of $TlClO_4$ extrapolated to infinite dilution.

^{13}C NMR spectra have been recorded at 100.6 MHz at a probe temperature of 25 $\pm$ 0.5 °C with a Bruker AM400 spectrometer. The NMR parameters were chosen so that quantitative spectra were obtained, typically flip angle 30° (3.5 µs), pulse repetition time 1 s,[14] spectral window 17 kHz, number of scans 15000–90000. The chemical shifts are accurate within ± 0.02 ppm and are reported in ppm toward higher frequency with respect to external TMS.

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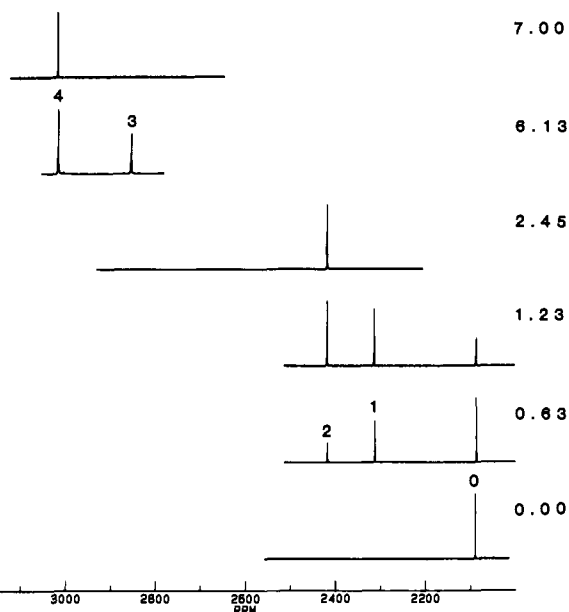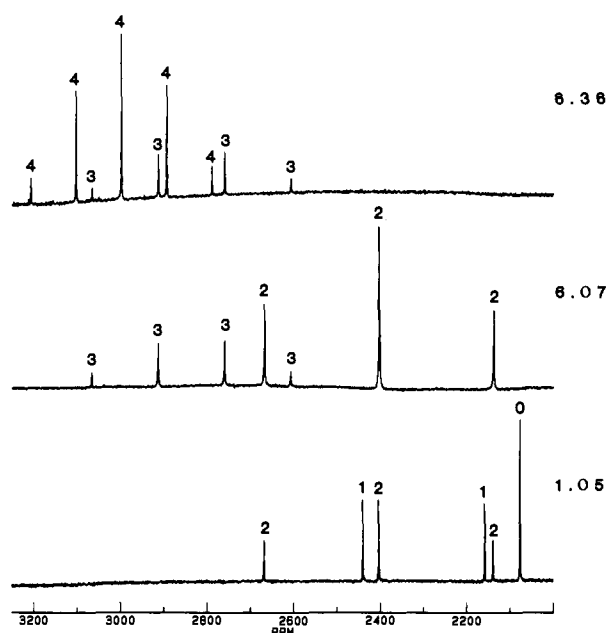(13) Irving, H. M. *Analyt. Chim. Acta* **1967**, *38*, 475.

Table I. Total Concentrations of Tl(III), CN⁻, and H⁺. ²⁰⁵Tl and ¹³C NMR Integrals for the Solutions Used for Determination of the Thallium–Cyanide Stability Constants

total concentrations[a]			Tl³⁺	TlCN²⁺		Tl(CN)₂⁺		Tl(CN)₃		Tl(CN)₄⁻		HCN
Tl	CN	H⁺	Tl	Tl	C	Tl	C	Tl	C	Tl	C	C
50.13	88.86	1479	6.63	9.31	6.23	18.4	42.2					3.76[c]
				10.01	4.67	37.2	43.1					
						18.5						
50.13	94.23	1448	4.9	8.61	4.70	18.7	43.4					4.9[c]
				9.23	5.19	38.6	41.8					
						19.9						
50.13	99.19	1418	2.4	6.38	3.2	20.9	44.1					2.93
				7.21	3.7	42.0	43.6					2.4
						21.18						
50.18	304.6	206.0				18.5	13	3.5	6.17			31.1
						37.2	12.2	9.63	6.78			30.9
						18.5		9.22				
								3.5				
50.19	311.1	167.3					4.03		16.0		3.26	26.6
							4.30		16.2		3.82	25.8
50.19	315.6	141.1				0.93	1.0	6.61	12.1	2.7	15	22.5
						1.7	d	18.9	12.5	11.5	15.1	21.6
						0.70		19.5		17.3		
								6.10		11.7		
										2.4		
49.49	25.89	1841	57.9	12.6	25.9	3.4	26.0					1.2[c]
				13.6	22.7	9.0	24.2					
						3.4						
49.44	51.77	1685	34.5	14.4	15.2	8.4	35.3					2.6[c]
				15.7	15.2	17.7	31.8					
						9.3						
49.37	82.83	1498	10.8	13.30	7.3	14.7	42.3					3.3[c]
				11.7	7.3	33.5	39.8					
						16.0						
48.98	258.85	435.2				22.7	19.8	d	0.48			29.8
						46.27	18.7	0.57	0.55			30.7
						23.1		0.71				
								0.24				
48.91	289.91	247.7				22.5	15.7	1.32	2.47			32.1
						45.8	14.6	3.36	2.60			32.5
						22.3		3.75				
								1.08				
48.88	300.27	185.2				15.3	9.47	5.7	10.9	0.86[e]		28.9
						28.6	9.50	15.0	11.3	0.86		28.2[e]
						14.3		15.2				
								5.9				
48.86	310.62	122.7						3.29	5.38	4.9	24.42	20.6
								9.03	5.44	18.8	24.45	19.7
								9.52		28.6		
								2.33		18.7		
										4.7		

[a] In mM. [b] Integrals in % of total integral area. [c] Peaks in the HCN doublet could not be integrated separately. [d] No peak found. [e] One of the ¹³C peaks for Tl(CN)₄⁻ and the peak for HCN were overlapping and hence could not be integrated separately. The integral for Tl(CN)₄⁻ has been set to the same value as the other (i.e., coupled) Tl(CN)₄⁻ peak, and this value has been subtracted from the total integral of the two peaks to give the integral for the HCN peak.

Table II. Overall Stability Constants, Individual ²⁰⁵Tl and ¹³C Chemical Shifts, and Spin–Spin Coupling Constants for Tl(CN)$_n^{3-n}$ Complexes, HCN, and CN⁻ [a]

species	log β[b]	²⁰⁵Tl shift[c,d]	δ(¹³C)[e,f]	J(²⁰⁵Tl–¹³C)[g]	J(¹H–¹³C)[g]	J(²H–¹³C)[g]
Tl³⁺		2087.5				
TlCN²⁺	13.21 (11)	2310.0	141.21	14 636 (53)		
Tl(CN)₂⁺	26.50 (18)	2414.4	141.97	13 749 (17)		
Tl(CN)₃	35.17 (19)	2848.4	147.40	7 954 (3)		
Tl(CN)₄⁻	42.61 (22)	3010.0	144.98	5 436 (4)		
HCN	10.11 (5)[h]		114.98		270.6 (1.7)	41 (±1)[i]
CN⁻			167.4			

[a] Temperature, 25 °C; ionic medium, [Na⁺] = 1 M, [Li⁺] + [H⁺] = 3 M, [ClO₄⁻] = 4 M. Estimated standard deviations (3σ) are given in parentheses. [b] β = [Tl(CN)$_n^{3-n}$]/([Tl³⁺][CN⁻]^n). [c] In ppm toward higher frequency with respect to an aqueous solution of TlClO₄ extrapolated to infinite dilution. [d] The experimental values of the shifts varied within ±0.7 ppm in different solutions. [e] In ppm toward higher frequency with respect to TMS. [f] The experimental values of the shifts varied within ±0.1 ppm in different solutions. [g] In Hz. [h] K = [HCN]/([H⁺][CN⁻]). [i] Measured for a solution containing 1 M NaCN and 2 M DClO₄ in D₂O; estimated error in parentheses.

¹⁴N NMR spectra have been recorded at 28.9 MHz at a probe temperature of 25 ± 0.5 °C with a Bruker AM400 spectrometer. The NMR parameters were typically pulse width 40 μs, pulse repetition time 0.8 s, spectral window 20 kHz, number of scans 200–70000, and external 0.1 M MeNO₂ in CDCl₃ as spectrum reference.

Results and Calculations

Spectra. The ¹³C and ²⁰⁵Tl NMR spectra, some of which are presented in Figures 1–3, show that we have slow exchange on the actual NMR time scale for both nuclei. This means that each
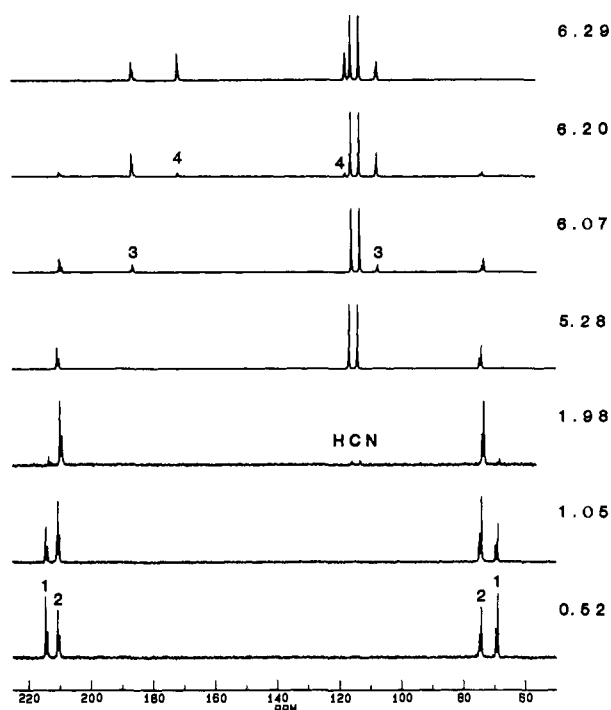
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Figure 3. 100.6-MHz ^{13}C NMR spectra for ^{13}C-enriched solutions for different $[CN^-]_{tot}/[Tl^{3+}]_{tot}$ ratios. The numbers over the peaks denote n in $Tl(CN)_n^{3-n}$. The chemical shifts are given in ppm toward higher frequency with respect to TMS.

complex gives rise to one peak (with splittings) whose area is proportional to the concentration of that complex. Each peak in the ^{13}C spectra is split into four peaks since natural thallium consists of two spin = $^1/_2$ isotopes, ^{203}Tl and ^{205}Tl (abundance ratio = $^3/_7$) with different spin–spin coupling constants to ^{13}C (the ratio between their spin–spin couplings to ^{13}C is equal to the ratio between their magnetogyric factors, i.e., 0.990). The peak of HCN is split into two peaks due to the ^{13}C–^{1}H coupling. Since we have slow exchange, all the shifts and spin–spin couplings for the thallium complexes can be determined directly from the spectra and are given in Table II. The individual ^{13}C chemical shifts of the species HCN and CN$^-$ were determined by adding H$^+$/OH$^-$ to a solution of NaCN in the ionic medium until the shift did not change any more. The line widths were ~40 Hz for ^{205}Tl NMR and ~10 Hz for ^{13}C NMR. The latter signals are considerably broader than the corresponding signals obtained previously for several cyano complexes;[15] for possible causes of this behavior, cf. ref 14. The experimental data, i.e., the total concentrations

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(14) We have determined that these parameters are good for recording quantitative spectra. It might seem that our pulse repetition time is short compared to the previously determined ^{13}C relaxation times (T_1) for different cyanide complexes in aqueous solutions.[15,16] For example, T_1 has been determined to be ≈7.5 s for CN$^-$ (0.1 M), for the Hg(CN)$_2$ complex (saturated solution), and for another complex suggested to have the composition Hg$_2$-(CN)$_2^{2+}$ (samples in D$_2$O, not degassed, not recrystallized)[16] and 56 s for the Hg(CN)$_4^{2-}$ complex (samples in D$_2$O, degassed, recrystallized).[15] There might be some reasons why the relaxation times in our solutions are much shorter: (1) the solutions were not degassed (paramagnetic O$_2$ is present), (2) the chemicals were not recrystallized and could contain trace amounts of paramagnetic impurities, (3) the solvent in our case was H$_2$O (and not D$_2$O), which may cause more efficient dipole–dipole relaxation, (4) in the presence of the directly bonded spin = $^1/_2$ nucleus, intramolecular dipole–dipole relaxation should be quite efficient; certainly, this was not the case for Pt(CN)$_4^{2-}$ complex,[15] but for platinum the abundance of the spin = $^1/_2$ nucleus is only 33% and for thallium 100%; moreover, both of the Tl isotopes (^{203}Tl and ^{205}Tl) are stronger magnets than ^{195}Pt; (5) chemical exchange between the Tl(CN)$_n^{3-n}$ complexes and the CN$^-$ or HCN, provided that the latter molecules have shorter T_1. Thus, even if scalar relaxation of the second kind due to rapid relaxation of ^{14}N has been postulated to be the dominating relaxation mechanism for ^{13}C in several cyano complexes,[15] one or probably a combination of the above mentioned factors can be responsible for the shortening of the relaxation times in our solutions.

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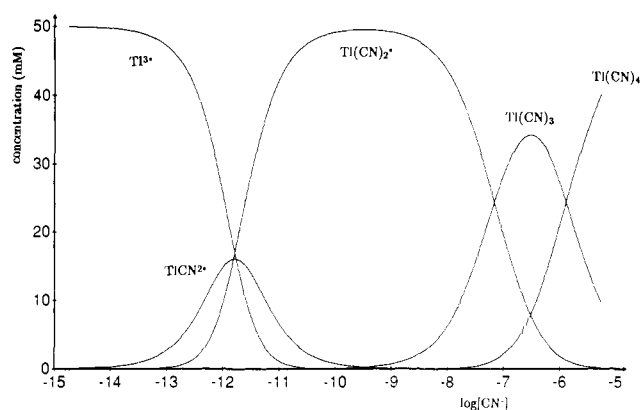

Figure 4. Distribution of the $Tl(CN)_n^{3-n}$ complexes as calculated from the determined stability constants using the same total concentrations as in the NMR measurements.

of the components and the peak integrals used for the determination of the equilibrium constants, are given in Table I.

^{14}N NMR spectra were much less informative because the signals were usually some kilohertz broad due to the quadrupolar relaxation of the ^{14}N nucleus and probably also due to chemical exchange. The signals of the free cyanide ion (−112 ppm) and HCN (−141 ppm) were, however, much narrower (about 50–100 Hz).

Determination of the Equilibrium Constant for HCN. In order to determine the acid constant, we gradually added HClO$_4$ to a 50 mM solution of Na^{13}CN in the ionic medium while measuring pH and recording ^{13}C spectra. Since we have in this case fast chemical exchange between HCN and CN$^-$, we obtain only one peak with a chemical shift that is a direct function of the individual chemical shifts of HCN and CN$^-$ and the relative amounts of these species:

$$\delta_{obs} = \delta_{HCN}p_{HCN} + \delta_{CN^-}p_{CN^-}$$

Substituting this into the acid constant and re-forming gives

$$pK_a = pH + \log\left[(\delta_{CN} - \delta_{obs})/(\delta_{obs} - \delta_{HCN})\right]$$

The resulting stability constant for HCN as well as the individual chemical shifts for the species HCN and CN$^-$, δ_{HCN} and δ_{CN}, respectively, are given in Table II.

Determination of Stability Constants for $Tl(CN)_n^{3-n}$, $n = 1-4$. The four stability constants, $\beta_1-\beta_4$, were least-squares fitted to the peak integrals from ^{205}Tl and ^{13}C NMR spectra and the material balances for each solution, i.e.,

$$[Tl^{3+}]_{tot} = \sum_0^n [Tl(CN)_n^{3-n}]$$

$$[CN^-]_{tot} = [HCN] + [CN^-] + \sum_0^n n[Tl(CN)_n^{3-n}]$$

$$[H^+]_{tot} = [H^+] + [HCN]$$

with the computer program LAKE.[17] The results are given in Table II, and the distribution of the complexes is given in Figure 4. The mean relative error in the ^{205}Tl NMR peak integrals was calculated to be about 3%. A similar value was obtained for the ^{13}C integrals, except for the few cases where the species HCN was present in very small concentrations, leading to a considerably higher relative error for the integral of the small doublet peak of HCN.

Discussion

It is easy to see (Figure 1) that, besides the expected ^{205}Tl NMR peak at ~2100 ppm, representing Tl^{3+}(aq),[18] four other Tl(III)–CN$^-$ species are formed. It can be proved by means of ^{205}Tl NMR

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for solutions where ^{12}C has been replaced by ^{13}C (Figure 2) that the other four species are $Tl(CN)_n{}^{3-n}$, $n = 1-4$. (Since both ^{205}Tl and ^{13}C nuclei possess magnetic moments (spin $= ^1/_2$), the $^{205}Tl-^{13}C$ spin–spin couplings cause each complex to give rise to $(n + 1)$ peaks with intensities of the multiplet following the binomial coefficients.) We have tried to check the possibility that higher complexes (e.g., with $n = 5$ or 6) may form in this chemical system. However, increasing the CN/Tl ratio up to 40 and decreasing the acid concentration did not result in new peaks in ^{205}Tl NMR spectra, and the shift of the $Tl(CN)_4{}^-$ signal changed only a few ppm before a lot of blue or brown precipitate occurred (hydrolysis products?). Taking into account the high sensitivity of the ^{205}Tl NMR method, we can conclude that, if any higher complex exists at all, its concentration in the investigated solutions is less than 1% of that of $Tl(CN)_4{}^-$ and, hence, its stepwise formation constant can be roughly estimated to be lower than 10^{-2}.

The redox potentials for the reactions

$$Tl^{3+} + 2e^- \rightleftharpoons Tl^+ \qquad e^0 = 1.25 \ V^{2b}$$

$$(CN)_2 + 2e^- \rightleftharpoons 2CN^- \qquad e^0 = 0.27 \ V^{19}$$
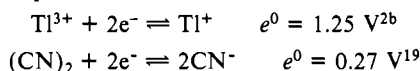
lead to the equilibrium constant

$$[(CN)_2][Tl^+]/([Tl^{3+}][CN^-]^2) = 10^{33.1}$$

It is true that the thallium–cyanide complexes are strong, but if we consider the equilibrium constant for the reduction of Tl^{3+} together with Figure 4, it becomes clear that Tl^{3+} cannot be thermodynamically stable at any cyanide/thallium ratio. Nonetheless, the solutions have proven to be quite stable. One could think, that the large polarizability of the cyanide ion leads to decreased positive charge on the thallium ion and this fact reduces the oxidizing power of thallium(III) so much that it is stable in the strong cyano complexes. However, such an effect would also lead to an increased shielding of the thallium nucleus and hence would decrease the ^{205}Tl NMR chemical shifts for the cyano complexes as compared to the $Tl(H_2O)_6{}^{3+}$ ion. As can be seen from Table II or Figure 1, the trend of the chemical shifts is the opposite.

Thus, the reason for the stability of the $Tl(CN)_n{}^{3-n}$ complexes is obviously their kinetic inertness. It is generally assumed that reduction–oxidation reactions often consist of several elementary, one-electron steps.[20] This assumption is based on the proposition that the transfer of several electrons in a single elementary discharge act is less probable than the sequential transfer through one-electron intermediate steps. In the present case, the reaction

$$Tl(III) + CN^- \rightleftharpoons Tl(II) + CN^• \qquad (2)$$
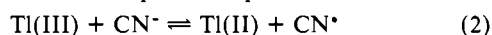
can be considered as the first step of the reduction of thallium(III). (In fact, formation of the instable Tl(II) from Tl(III) and an aquated electron has been observed and studied.[21]) The standard potential for the couple Tl^{3+}/Tl^{2+} in 1 M $HClO_4$ has been estimated to be 0.3 V.[20b] For $CN^•/CN^-$, the standard potential is ~ 2.5 V,[22] which recalculated to acidic solution (1 M $HClO_4$) gives ~ 3.0 V (using $pK_a(HCN) = 9.0$). This means that the reaction above would *not* be energetically favorable. The standard potential for the couple Tl^{2+}/Tl^+ is 0.95 V so that also here the one-electron transfer step

$$Tl^{2+} + CN^- \rightleftharpoons Tl^+ + CN^• \qquad (3)$$
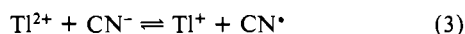
is energetically unfavorable. The stability constants for cyano complexes of Tl(II) are unknown but are probably much weaker than those for Tl(III) (cf. ref 21 for the corresponding chloride complexes, which are about 2 orders of magnitude weaker for Tl(II) than for Tl(III)). Thallium(I) does not form cyano complexes.[23] Concluding, if one of the two reactions 2 and 3 discussed above is rate determining, the reduction of Tl(III) by CN^- (re-
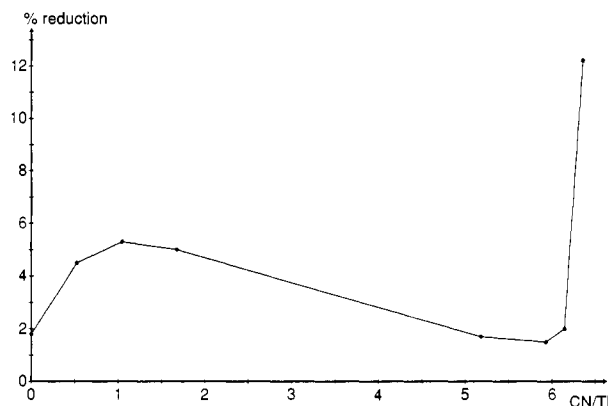
% reduction

Figure 5. Reduction of Tl(III) to Tl(I) in percent of the total thallium concentration in 1-year-old solutions (kept at room temperature) containing 50 mM thallium and different CN/Tl ratios.

action 1) will be kinetically hindered and, accordingly, $Tl(CN)_n{}^{3-n}$ complexes will be stable.

In order to roughly estimate the rate of reduction of thallium-(III) to thallium(I) in cyanide solutions, we have analyzed solutions kept at room temperature for 1 year and containing 50 mM Tl(III) and varying amounts of cyanide and perchloric acid. Only a limited reduction of Tl(III) was found. The concentration of Tl(I), which was less than 1% of the total thallium in the beginning of the experiment, increased to between 2% and 5% in solutions with low CN/Tl ratios (and high acidity) and to about 12% in solutions where CN/Tl was higher than 6 and pH > 4 (cf. Figure 5). This is in accordance with the results of Penna-Franca and Dodson,[7] who found a drastic increase of the rate of the Tl(III)–Tl(I) exchange reaction with increasing CN^- concentration.

After several months at room temperature, we also found a decrease of $[CN^-]_{tot}$ in solutions with high $[CN^-]_{tot}/[Tl^{3+}]_{tot}$ ratios, and a new signal appeared in the ^{14}N NMR spectra (at 364.9 ppm, $\Delta\nu_{1/2} = 3$ Hz, pentet with the intensity ratio about 1:4:6:4:1, $^1J(^{14}N-^1H) = 53$ Hz), which we assigned to be due to some formation of $NH_4{}^+$. We also found formic acid with ^{13}C NMR. This is not surprising since it is well-known that aqueous solutions of simple cyanides (e.g., NaCN) decompose to give ammonium ions and formic acid.

Stability Constants. The determined numerical values of the stability constants of the $Tl(CN)_n{}^{3-n}$ complexes (Table II) are not exactly in accordance with the value $K_2/K_1 = 0.15$ suggested by Penna-Franca and Dodson[7] nor with the value of log $\beta_4 = 35$ calculated[10] on the basis of the data of Spencer and Abegg.[9] However, even if the latter two numbers were obtained many years ago and in an indirect way, it is possible that the agreement can be considered as satisfactory if the effect of the different ionic media is taken into account.

The stability constant for HCN determined in this work, log $K_a = 10.11$ (2), cannot be compared directly to the literature data since the constant has not been determined previously for the actual ionic medium.[4] However, the value of this constant in, e.g., 3 M $NaClO_4$ has been determined by means of two independent emf measurements and found to be, respectively, log $K_a = 8.81$ (± 0.03) (glass and cyanide electrodes)[24] and 9.48 (± 0.01) (glass electrode).[25]

The so-called constant ionic medium method,[26] i.e., the use of a concentrated solution of an inert salt (often alkali perchlorate), proves to be a necessary condition for the study of complicated ionic equilibria. The method is based on the fact that, in an inert electrolyte solution of high and constant concentration, the variations of activity coefficients are kept at a minimum provided the concentration of the medium salt by far exceeds that of the reagent species. The ionic medium in the present work ($[Na^+]$

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Table III. Stepwise Stability Constants (log K_n) for Cyano Complexes of d^{10} Ions. Temperature 25 °C

	M(CN)	M(CN)$_2$	M(CN)$_3$	M(CN)$_4$	ionic medium	ref
Cu(I)		21.7^a	5.1	1.1	~0^b	30
Ag(I)		20.9^a	0.9		0	30
Au(I)		39^a			approx value	31
Zn(II)	5.3	5.7	6.7	4.9	3 M NaClO$_4$	25
Cd(II)	5.6	5.2	4.9	3.5	3 M NaClO$_4$	25
Hg(II)	17.0	15.8	3.6	2.7	0	32
Tl(III)	13.2	13.3	8.7	7.4	1 M NaClO$_4$ + 3 M (Li + H)ClO$_4$	this work

^{a} β_2. ^{b} 22 °C.

= 1 M, [Li$^+$] + [H$^+$] = 3 M, [ClO$_4^-$] = 4 M) was chosen so that the determined stability constants would be directly comparable to the previous determinations of stability constants for thallium(III)–halide complexes performed in 3 M HClO$_4$ + 1 M NaClO$_4$.[18,27] It is known from the specific interaction theory calculations that replacement of Li$^+$ by H$^+$ does not change the interaction coefficients and accordingly has no influence on the values of the equilibrium constants.[28] It has been argued[29] that LiClO$_4$ should not be used as an ionic medium because of the possibility of complex formation between the lithium ion and the investigated ligand. We have controlled this possibility by titration of a solution containing 0.1 M NaCN by small amounts of solid LiClO$_4$·3H$_2$O and measuring the ^{13}C NMR chemical shift after each addition. The chemical shift was not changed significantly for lithium concentrations varying between 0 and more than 4 M. Although some trivial explanations are possible (e.g., the chemical shift of the LiCN complex is very close to the shift of the free CN$^-$ ion), we take this fact as an indication that no strong complex formation takes place between lithium and cyanide. Still, even if the complex would exist and have as high stability constant as K = 1 M^{-1} (suggested by Hefter[29] for the complex LiF), it would have no detectable influence on the determined stability constants for the extremely strong Tl(CN)$_n^{3-n}$ complexes.

The Tl(CN)$_n^{3-n}$ complexes are stronger than any other known monodentate complexes of thallium(III). There is only one exception, namely TlI$_4^-$, whose overall stability constant, log β_4 = 35.0,[5] is close to that of Tl(CN)$_4^-$.

Stepwise stability constants for MX$_n$ complexes often decrease with increasing n because of statistical, steric, and Coulombic factors.[3b] There are, however, some exceptions such as the cyanide complexes of the d^{10} ions copper(I), silver(I), probably gold(I), and mercury(II) where the extreme stability of the second complex, MX$_2$, breaks the decreasing trend. Thallium(III) ion, which is isoelectronic with Au(I) and Hg(II), behaves in a similar way (cf. Table III). It is certainly not a coincidence that also diorganothallium(III) compounds containing the linear C–Tl–C group are extremely stable;[2,33] for example, the Tl(CH$_3$)$_2^+$ ion is stable in aqueous solution.[34]

There is some evidence that back-donation plays an important role in cyano complexes.[35] For isoelectronic Au(I), Hg(II), and Tl(III), the back-donation should be most efficient (and hence the complexes should be strongest) for gold and least efficient for thallium because of the increasing charge on the metal. If the back-donation is a major 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 (approximately) known for gold(I), but there is no doubt that the β_2 values follow the predicted trend

$$\log \beta_2 = 39 \text{ (for Au)}^{31} > 32.7 \text{ (for Hg)}^4 > 26.7 \text{ (for Tl)}$$

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 13.2, respectively. However, in the tricyano and tetracyano complexes of these two metal ions, the opposite trend is found. This might indicate that in the latter two complexes the back-donation is less important compared to other factors. Indeed, the enthalpy of the formation of the Hg(CN)$_3^-$ and Hg(CN)$_4^{2-}$ complexes is 3 times smaller than for the species Hg(CN)$^+$ and Hg(CN)$_2$,[32] which might be indicative of a decreasing covalent contribution for the tri- and tetracyano complexes. Still, this is only one possible explanation and certainly not the only one (cf., e.g., the discussion of the ^{13}C chemical shifts in ref 15).

Since the vast majority of the known stability constants has been determined by means of potentiometric measurements, it can be of interest to compare the precision of our determination to that of the traditional method. Thus, for example, the error in the stability constants for the complexes TlX$_n^{3-n}$ (X = Cl, Br) determined by Ahrland et al.[27] using potentiometry was estimated by the authors to be 0.05–0.06 logarithmic units. The corresponding value for the Hg(CN)$_n^{2-n}$ complexes varies between 0.01 and 0.08 logarithmic units.[32] This can be compared to our value of 1 standard deviation amounting to 0.03–0.07 logarithmic units, i.e., the same order of magnitude. For log K_a(HCN), 1 standard deviation in the acid constant determined in this work is 0.02 units compared to the error ± 0.03 given in ref 24 (potentiometric determination). Hence, the precision of the two methods is comparable. This fact does not, however, say anything about the accuracy of the methods. The latter will be discussed in a forthcoming paper.

Inexpensive equipment favors the traditional method. On the other hand, the NMR method gives in favorable cases (like the present one) not only the numerical values but also direct evidence for the composition of the studied complexes as well as structural information from the NMR parameters.

Chemical Shifts. The carbon-13 chemical shifts for the Tl(CN)$_n^{3-n}$ complexes (cf. Table II) fall in the same range as the shifts for the corresponding complexes of other d^{10} ions, like Cu(I), Ag(I), Au(I), Zn(II), Cd(II), or Hg(II), i.e., about 140–162 ppm.[15,36] The normal decrease of the chemical shift with increasing charge of the central atom, previously interpreted as to be determined by differences in the M–C σ-bond contributions,[19b] is valid also for thallium(III): for the linear complexes Au(CN)$_2^-$, Hg(CN)$_2$, and Tl(CN)$_2^+$,[37] the shifts are 154.2, 144.6, and 141.97 ppm,[39] respectively, and for the tetrahedral complexes Hg(CN)$_4^{2-}$

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(37) The complexes Au(CN)$_2^-$ and Hg(CN)$_2$ are generally accepted to be linear and the complex Hg(CN)$_4^{2-}$ is tetrahedral;[38] the assumption that also Tl(CN)$_2^+$ is linear and Tl(CN)$_4^-$ is tetrahedral comes from a preliminary Raman spectroscopic study, currently being performed in this laboratory in cooperation with Dr. M. Sandström.

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and $Tl(CN)_4^-$,[37] the corresponding shifts are 153.2 and 144.98 ppm.[39]

Another trend was observed by Hugel et al.[40] for cyano complexes of copper(I). As the number of ligands increased from two (linear $Cu(CN)_2^-$) to three (trigonal–planar $Cu(CN)_3^{2-}$) and four (tetrahedral $Cu(CN)_4^{3-}$), the Cu–CN distance increased (1.88, 1.95, 2.00 Å, respectively) and the ^{13}C chemical shift increased (149.2, 156.2, 161.9 ppm). Although no distances are known for the thallium–cyanide complexes, the trend in the ^{13}C chemical shifts is the same for the first, second, and third complexes, whereas the last complex, $Tl(CN)_4^-$, has its shift lower than $Tl(CN)_3$ but still higher than $Tl(CN)_2^+$. The difference may be caused by the different structure of the $Tl(CN)_3$ complex as compared to $Cu(CN)_3^{2-}$.

Rationalization of the ^{13}C chemical shifts of carbon atoms bonded to metal ions has been discussed in a large number of papers.[41] However, as pointed out by Evans and Norton,[41] no convincing explanation for the shifts has been found. There are several factors influencing the chemical shifts, and any discussion concerning only one of these is not likely to be useful or correct.[15]

There is no obvious correlation between the ^{205}Tl chemical shifts for the thallium(III)–cyano complexes and for the corresponding halo complexes. Certainly, the values of $\delta(Tl(CN)_n^{3-n})$, $n = 1–4$, follow a similar trend as the corresponding values for the $TlCl_n^{3-n}$ complexes[18] and CdX_n^{2-n} (X = Cl, Br, I) complexes.[42] The octahedral complexes ($M(H_2O)_6$, MX, MX_2, MX_5, and MX_6— water molecules and charges are omitted for clarity) are more shielded than the tetrahedral ones (MX_4). There is an increase of the shift from the hydrated metal ion, $M(H_2O)_6$, to the $M(H_2O)_nX$ complex, a smaller change between the mono- and dicomplexes, and then larger frequency changes to the third and to the fourth complexes. Still, one would rather expect a closer similarity between the shifts for the thallium cyanide complexes and for the thallium complexes of the heavier halides because of their "soft" character.[43] The comparison of the Tl NMR shifts for the thallium chloride, bromide, iodide[18] (for the iodide complexes only $\delta(TlI_4^-)$ is known, −1764 ppm, in CH_2Cl_2 solution[18]), and cyanide complexes shows clearly that the chemical shifts are governed by several parameters. One of the most important parameters is certainly the structure of the complex, but even for the probably isostructural complexes TlX^{2+}, TlX_2^+ (X = Cl, Br, CN), and TlX_4^- (X = Cl, Br, I, CN), it is not easy to propose any simple rationalization of their chemical shifts. Another important parameter is the "heavy atom shift"[44] which is smaller for complexes of the metals in the 3d and 4d series of the periodic system and larger for the 5d series.[45a] The heavy atom shift probably causes the big shifts to lower frequency for TlI_4^- and $TlBr_6^{3-}$[18] but not for $TlCl_4^-$, $TlCl_6^{3-}$,[18] and $Tl(CN)_4^-$. In the case of cyano complexes, an additional parameter is probably of importance, namely, the back-donation of the electron density from the metal to the cyanide. The back-donation will cause lower shielding of the thallium nucleus and hence an increase in the metal NMR chemical shift. On the other hand, σ-bonding contribution will have the opposite influence. It would be interesting to compare the changes in the ^{205}Tl NMR chemical shifts for the different cyanide complexes (Table II) to the corresponding changes in the metal NMR chemical shifts for mercury(II) and for the other d^{10} ions. Unfortunately, metal NMR data on the latter complexes are rather scarce.[19,38,45b]

Spin–Spin Coupling Constants. One-bond coupling constants between thallium and carbon, $^1J(^{205}Tl-^{13}C)$, can vary in the range

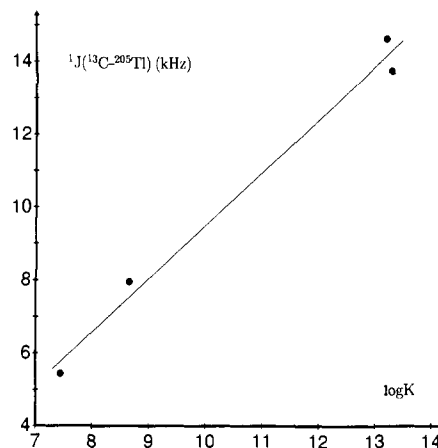**Figure 6.** Correlation between the $^{205}Tl-^{13}C$ spin–spin coupling constants for the $Tl(CN)_n^{3-n}$ complexes and their stepwise stability constants.

from less than 2000 Hz for triorganothallium(III) to 2100–5800 Hz for diorganothallium to 6000–10700 Hz for monoorganothallium compounds.[46] The coupling constants for the mono- and dicyano complexes of thallium(III) are well above this range (cf. Table II) and appear to be the largest known coupling constants between these nuclei. The corresponding constants for the tri- and tetracyano complexes are much smaller and fall in the range of mono- and diorganothallium(III) compounds.[46]

Spin–spin coupling constants between two nuclei mirror, among others, the distance and hence the strength of the bond between them. Hence, the large values of the $^1J(^{205}Tl-^{13}C)$'s for the $Tl(CN)_n^{3-n}$ complexes compared to the organothallium(III) compounds with the same number of thallium–carbon bonds are noteworthy and indicate that the Tl–C bonds in the cyanides are probably the strongest bonds thallium(III) can form at all, at least at the present level of our knowledge. If the strength of the thallium–carbon bonds is the main factor determining the size of the Tl–C coupling constants, then we should expect a strong correlation between the latter and the stability constants for the corresponding $Tl(CN)_n^{3-n}$ complexes, at least if the cyanide ion is bonded to thallium via the carbon atom. This is also what we find; in fact, the plot of the logarithms of the stepwise formation constants for the thallium(III)–cyanide complexes versus the corresponding $^{205}Tl-^{13}C$ spin–spin coupling constants is almost linear (Figure 6). This can be seen as indirect evidence that, similarly to what is known about cyanide complexes of other metal ions, in all the $Tl(CN)_n^{3-n}$ species thallium is bonded to the carbon and not to the nitrogen atom of the cyanide ion.

The $^1H-^{13}C$ coupling constant for the $H^{13}CN$ molecule, 270.6 (1.7) Hz, determined in this work, can be compared to the values of 274 (1),[47] 269,[48] or 267.3 (1) Hz[49] determined previously for neat HCN. This may indicate that the strong H–C bond in HCN is neither significantly influenced by the surrounding water molecules nor by the four molar ionic medium (including large amounts of free acid) present in our solutions. The $^2D-^{13}C$ coupling constant in $^2D^{13}C^{14}N$ determined in this work, 41 (±1) Hz, is in agreement with the corresponding constant determined for neat $^2D^{13}C^{15}N$, 40.95 (10) Hz.[49] This is also the case with $^1J(^2D-^{13}C) = 41.5$ (3) Hz, calculated from the experimental value of $^1J(^1H-^{13}C)$.

Conclusions

Thallium(III)–cyanide complexes in solution should not exist according to the redox potentials, and in fact, their existence has never been proved before. However, considering the evidence

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presented in this paper, in our opinion there is no doubt that these complexes exist, that their composition is $Tl(CN)_n^{3-n}$, $n = 1$–4, and that they are extremely strong and stable. We are not able to find any good explanation why these complexes have not been established before in spite of the possibility to investigate this system by means of, e.g., emf measurements. The equilibria between the complexes are fast (on the real time scale), and it is not a difficult task to find a good thallium- and/or cyanide-sensitive electrode. There might be a possibility that the well-known toxicity of cyanide and thallium has had a prohibitive effect on presumptive investigators. On the other hand, it was pointed out already by Ostwald by 1897, who discussed the high stability of cyanomercaurate species, that "notwithstanding the extremely poisonous character of its constituents, it exerts no appreciable poison effect".[6b] Another possibility might be that the presumed reduction of Tl(III) by cyanide, suggested in an authoritative source of information on thallium chemistry,[2] prevented chemists from looking into this chemical system.

In spite of the fact that a large number of cyanide compounds have been prepared and investigated by different methods, there is lack of reliable thermodynamic studies concerning the stability of the complexes in solution, as was shown in the recent review article by Beck.[4] Because of the importance of the cyanide ion and its complexes in chemistry and in chemical industry (e.g., cyanide process for leaching of noble metals), it seems worthwhile to continue investigations of metal-ion cyanide complexes. The multinuclear NMR technique seems to be a useful tool for this purpose.

Synthesis and Electrochemical Studies of Catenates: Stabilization of Low Oxidation States by Interlocked Macrocyclic Ligands

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Abstract: The coordinating properties of a catenand, consisting of two interlocked 30-membered rings, have been studied. Several complexes, the catenates, have been prepared and fully characterized. The electron spectra of catenates have been measured, showing intense absorption bands in the visible for the Cu^I and Ni^I complexes. The strong color of copper(I) and nickel(I) catenates corresponds to a metal-to-ligand charge-transfer (MLCT) transition. Many of the catenates studied are strong photoemitters, the excitation light being in the near-UV or visible region. Both ligand-localized or MLCT excited states are responsible for the emission properties observed, depending on the metallic species complexed. The two 2,9-diphenyl-1,10-phenanthroline (dpp) subunits, which form the complexing species of the catenand, adopt an "entwined" geometry in all the catenates isolated. This special shape was clearly demonstrated by ^1H NMR studies for copper(I), silver(I), zinc(II), and cadmium(II) catenates and for their corresponding acyclic analogues containing two 2,9-di-p-anisyl-1,10-phenanthroline (dap) chelates. The molecular topography of the system in solution is thus in perfect agreement with the solid-state structure of copper(I) catenate, as earlier determined by X-ray crystallography. A detailed electrochemical study of the various catenates prepared has been carried out. The very general trend is that low oxidation states of transition-metal catenates are strongly stabilized. Some one-electron reductive processes have clearly been shown to occur on the ligand without decomposition of the complex. This is the case for lithium(I), copper(I), and zinc(II) catenates. It is even possible to generate stable solutions of the anionic copper complex by two-electron reduction of copper(I) catenate. In other instances, electron transfer takes place on the metal. The most straightforward situation is that of Ni^{II}, which is very readily reduced to Ni^I (d^9), this monovalent nickel catenate being surprisingly stable toward reoxidation. The nature of the orbitals involved in the reduction of Fe^{II}, Co^{II}, Ag^I, and Cd^{II} (ligand or metal centered) is not certain as yet. In any case, the destabilizing effect toward high oxidation states was so pronounced that it turned out to be impossible to generate trivalent states like Fe^{III} or Co^{III}. Rather, oxidation of the ligand part ($E > 1.4$ V versus SCE) was observed.

A new class of ligands, the **catenands**, has recently been developed.[1-4] A catenand consists of two or several interlocked coordinating macrocycles, the first member of this series containing two 30-membered rings. The particular class of catenands that has been synthesized and studied in our laboratories displays special coordinating properties due to the geometrical features of the ligands and their corresponding complexes. For clarity, we will consider two sets of geometrical properties: **topography** and **topology**.

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