Kinetics and Mechanism of Platinum–Thallium Bond Formation: The Binuclear [(CN)$_5$Pt–Tl(CN)]$^-$ and the Trinuclear [(CN)$_5$Pt–Tl–Pt(CN)$_5$]$^{3-}$ Complex

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Formation kinetics of the metal–metal bonded binuclear [(CN)$_5$Pt–Tl(CN)]$^-$ (**1**) and the trinuclear [(CN)$_5$Pt–Tl–Pt-(CN)$_5$]$^{3-}$ (**2**) complexes is studied, using the standard mix-and-measure spectrophotometric method. The overall reactions are Pt(CN)$_4^{2-}$ + Tl(CN)$_2^+$ ⇌ **1** and Pt(CN)$_4^{2-}$ + [(CN)$_5$Pt–Tl(CN)]$^-$ ⇌ **2**. The corresponding expressions for the pseudo-first-order rate constants are k_{obs} = (k_1[Tl(CN)$_2^+$] + k_{-1})[Tl(CN)$_2^+$] (at Tl(CN)$_2^+$ excess) and k_{obs} = (k_{2b}[Pt(CN)$_4^{2-}$] + k_{-2b})[HCN] (at Pt(CN)$_4^{2-}$ excess), and the computed parameters are k_1 = 1.04 ± 0.02 M^{-2} s^{-1}, k_{-1} = k_1/K_1 = 7 × 10^{-5} M^{-1} s^{-1} and k_{2b} = 0.45 ± 0.04 M^{-2} s^{-1}, K_{2b} = 26 ± 6 M^{-1}, k_{-2b} = k_{2b}/K_{2b} = 0.017 M^{-1} s^{-1}, respectively. Detailed kinetic models are proposed to rationalize the rate laws. Two important steps need to occur during the complex formation in both cases: (i) metal–metal bond formation and (ii) the coordination of the fifth cyanide to the platinum site in a nucleophilic addition. The main difference in the formation kinetics of the complexes is the nature of the cyanide donor in step ii. In the formation of [(CN)$_5$Pt–Tl(CN)]$^-$, Tl(CN)$_2^+$ is the source of the cyanide ligand, while HCN is the cyanide donating agent in the formation of the trinuclear species. The combination of the results with previous data predict the following reactivity order for the nucleophilic agents: CN$^-$ > Tl(CN)$_2^+$ > HCN.

Introduction

Four binuclear platinum–thallium cyano compounds and a trinuclear one containing direct metal–metal bonds that are not supported by ligands have been prepared in aqueous solution via reversible reactions of Tl(CN)$_n^{3-n}$ and Pt(CN)$_4^{2-}$ species. The general compositions of the binuclear and the trinuclear complexes are [(CN)$_5$Pt–Tl(CN)$_n$(aq)]$^{n-}$ (n = 0–3) and [(NC)$_5$Pt–Tl–Pt(CN)$_5$]$^{3-}$, respectively. The complexes have been identified and structurally characterized in solution by multinuclear NMR, EXAFS, and vibration spectroscopy.[1-3] These complexes feature transient oxidation

state metal centers, and they are surprisingly stable under certain conditions, in particular if the strong oxidative properties of thallium(III) are taken into account.[1,2] Studies on structural[1,2,4,5] and equilibrium[3] features, photochemical and thermal decomposition, and theoretical calculations[6,7a,b] of these complexes have previously been reported. A specific feature of the system is that the equilibration can be quite slow; it may require several hours to reach completion under acidic conditions. The formation kinetics of the [(NC)$_5$Pt–Tl(CN)$_3$]$^{3-}$ complex using spectrophotometric methods has recently been studied.[8] The overall order of the reaction Pt(CN)$_4^{2-}$ + Tl(CN)$_4^-$ ⇌ [(NC)$_5$Pt–Tl(CN)$_3$]$^{3-}$ is 3 in the alkaline region, which means first order for the two reactants and also for the [CN$^-$]. The mechanism includes a metal–

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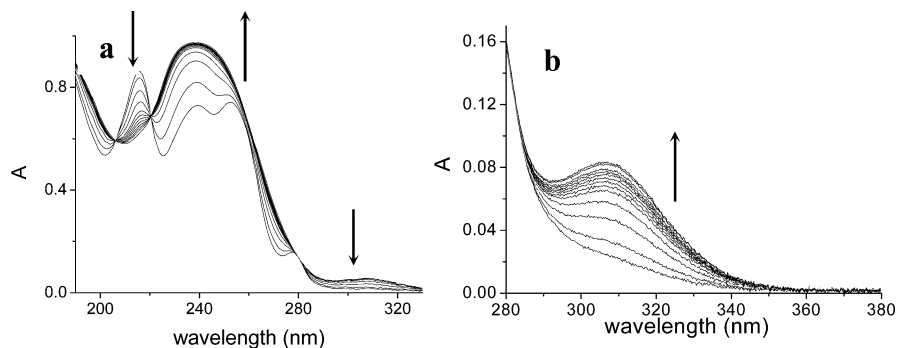
Figure 1. Spectral changes as a function of time during the formation of the (a) binuclear $[(CN)_5Pt-Tl(CN)]^-$ complex ($[Pt(CN)_4{}^{2-}] = 0.0025$ M; $[CN^-]_{tot} = 0.075$ M; $[Tl^{3+}]_{tot} = 0.030$ M initial concentrations; pH = 1.9; $l = 1$ mm; duration of the experiment 100 min) and (b) trinuclear $[(CN)_5Pt-Tl-Pt-(CN)_5]^{3-}$ complex ($[Pt(CN)_4]^{2-} = 0.060$ M; $[CN^-]_{tot} = 0.0142$ M; $[Tl^{3+}]_{tot} = 0.0050$ M initial concentrations; pH = 1.9; $l = 0.1$ mm, duration of the experiment 300 min).

metal bond formation step, the coordination of the axial cyanide to the platinum center, and finally the fast dissociation of the cyanide from the thallium center. The sequence of the first two steps could not be resolved, i.e., they may occur in reverse order. In this work we continue the investigation of the Pt−Tl bond formation and discuss the formation kinetics and mechanism of the binuclear $[(NC)_5Pt-Tl(CN)]^-$ and the trinuclear $[(NC)_5Pt-Tl-Pt(CN)_5]^{3-}$ complexes in detail.

Experimental Section

Materials. Solutions of $Tl(CN)_n{}^{3-n}$ and $Pt(CN)_4{}^{2-}$ were prepared as reported elsewhere.[8−11]

pH Measurements. pH values were measured by a combination electrode (Metrohm, 6.0234.100) connected to a pH meter (Radiometer PHM26). The pH meter readings were calibrated to −log [H+] values using the method of Irving et al.[12]

Kinetic Measurements.[13] Time-resolved UV−vis spectrophotometry is suitable to follow the metal−metal bond formation because these reactions are associated with characteristic spectral changes in the 200−360 nm wavelength range, see Figure 1. Kinetic measurements were made with a CARY 1E UV−visible spectrophotometer, using 1 cm, 0.1 cm, 0.02 cm, and 0.001 cm wide optical cells. Because of photochemical decomposition of the dinuclear and especially the even more sensitive trinuclear species, the continuous kinetic mode of the instrument was not suitable to follow the reactions. In such experiments the sample is exposed to a constant irradiation by the relatively high energy emission of the D-lamp. Therefore, the scanning mode of the spectrophotometer had to be used by parking the beam at 790 nm (where the species have no absorption) between cycles. The spectra were recorded in the wavelength ranges of 190−790 and 300−790 nm in the cases of the binuclear and the trinuclear complexes, respectively. The data were evaluated at wavelengths where the spectra of $Pt(CN)_4{}^{2-}$ and the metal−metal bonded complex are sufficiently different and

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(13) Throughout the paper square brackets, [ ], are used to indicate actual concentration in the kinetic equations or equilibrium concentrations in the formation constants when the charges are inside and mark complexes when the charges are outside.

the $Tl(CN)_2{}^+$ species has negligible contribution to the absorbance. The temperature was set to 25 °C in all cases and controlled by a LAUDA RM 20 thermostat. $Pt(CN)_4{}^{2-}$, $[(CN)_5Pt-Tl(CN)]^-$, and $[(NC)_5Pt-Tl-Pt(CN)_5]^{3-}$ exhibit intense absorption bands in the UV wavelength range ($\epsilon = 10^4-10^5$ M^{-1} cm^{-1}), and $[(NC)_5Pt-Tl-Pt(CN)_5]^{3-}$ also absorbs light in the visible region ($\lambda = 435$, $\epsilon = 22$ M^{-1} cm^{-1}), as indicated by the yellow color of the solutions.

The stability constants of the complexes studied are expressed as follows:[3]

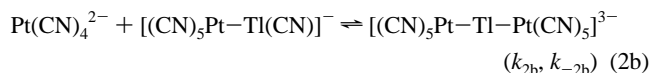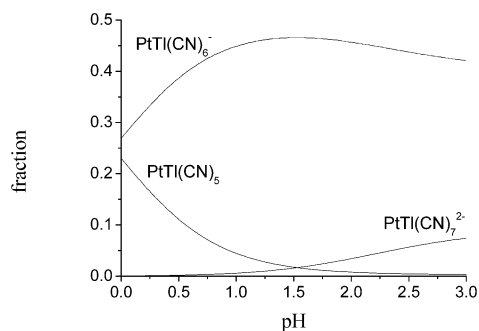$$Pt(CN)_4{}^{2-} + Tl(CN)_2{}^+ \rightleftharpoons [(CN)_5Pt-Tl(CN)]^- \quad (k_1, k_{-1}) \quad (1)$$

$$K_1 = \frac{[(CN)_5PtTl(CN)^-]}{[Tl(CN)_2{}^+][Pt(CN)_4{}^{2-}]} = 1.58 \times 10^4 \text{ M}^{-1}$$

In the presence of excess $[Pt(CN)_4{}^{2-}]$ a trinuclear species is formed:

$$2Pt(CN)_4{}^{2-} + Tl(CN)_2{}^+ \rightleftharpoons [(CN)_5Pt-Tl-Pt(CN)_5]^{3-} \quad (2a)$$

$$\beta_{2a} = \frac{[(CN)_5PtTlPt(CN)_5{}^{3-}]}{[Tl(CN)_2{}^+][Pt(CN)_4{}^{2-}]^2} = 3.98 \times 10^5 \text{ M}^{-1}$$

Actually, the formation of the trinuclear complex can also be described as follows:

$$Pt(CN)_4{}^{2-} + [(CN)_5Pt-Tl(CN)]^- \rightleftharpoons [(CN)_5Pt-Tl-Pt(CN)_5]^{3-}$$
$$(k_{2b}, k_{-2b}) \quad (2b)$$

$$K_{2b} = \frac{[(CN)_5PtTlPt(CN)_5{}^{3-}]}{[(CN)_5PtTl(CN)^-][Pt(CN)_4{}^{2-}]} = 25 \text{ M}^{-1}$$

Due to the small value of K_{2b}, a large excess of $[Pt(CN)_4{}^{2-}]$ was used to maintain high conversion for the trinuclear complex.

Concentration Ranges. (a) Formation Kinetics of $[(CN)_5Pt-Tl(CN)]^-$. (i) $[Tl(CN)_2{}^+]$ Dependence. $[Tl^{3+}]_{tot} = 0.02-0.045$ M; $[CN^-]_{tot} = 2.5[Tl^{3+}]_{tot}$; at constant 0.0025 M $[Pt(CN)_4{}^{2-}]_{tot}$ and pH = 1.90. Kinetic traces were evaluated at both 239 and 215 nm, on the absorption band of the $[(CN)_5Pt-Tl(CN)]^-$ and the $Pt(CN)_4{}^{2-}$ complexes, respectively.

(b) Formation Kinetics of $[(CN)_5Pt-Tl-Pt(CN)_5]^{3-}$. (i) Using $Pt(CN)_4{}^{2-}$ and $Tl(CN)_2{}^+$ Reactants. $[Tl^{3+}]_{tot} = 0.02$ (a, b), 0.016 (c) M; $[CN^-]_{tot} = 2.5[Tl^{3+}]_{tot}$; $[Pt(CN)_4{}^{2-}]_{tot} = 0.13$ (a), 0.1 (b, c) M; and pH = 3. Kinetic traces were evaluated at 344 nm, which corresponds to the bottom part of the characteristic absorbance band of the trinuclear species. These conditions were necessary to keep

Figure 2. Typical concentration distribution of the Pt containing species in aqueous solution as a function of pH. The calculations were made with stability constants taken from ref 3. $[Pt(CN)_4]^{2-} = 0.0025$ M, $[Tl^{3+}]_{tot} = 0.035$ M, and $[CN^-]_{tot} = 0.0847$ M.

the absorbance values in the 0.1−1 region and to have significant conversion at the same time. Measurements in thinner than 1 mm cells led to technical complications, and the observed data were not reproducible.

(ii) Using Pt(CN)₄²⁻ and [(CN)₅Pt−Tl(CN)]⁻ Reactants: [Pt(CN)₄²⁻] Dependence. $[Pt(CN)_4^{2-}]_{tot} = 0.05-0.17$ M; with $[(CN)_5Pt-Tl(CN)^-]_{tot} = 0.0041$ M ($[Tl^{3+}]_{tot} = 0.005$, $[CN^-]_{tot} = 0.0142$) and pH = 1.9. Kinetic traces were evaluated at 338 nm for the same reason mentioned above.

(iii) Cyanide Dependence. With constant $[Pt(CN)_4^{2-}]_{tot} = 0.0909$ M; $[Tl^{3+}]_{tot} = 0.0033$ and with different $[CN^-]_{tot} = 0.00807-0.0207$ ($[HCN] = 0.0015-0.0142$) and pH = 1.34−2.20.

The "absorption−time" curves were fitted by Microcal Origin curve fitting routine.[14] All experimental rate constants were fitted simultaneously by the Micromath Scientist data fitting program.[15]
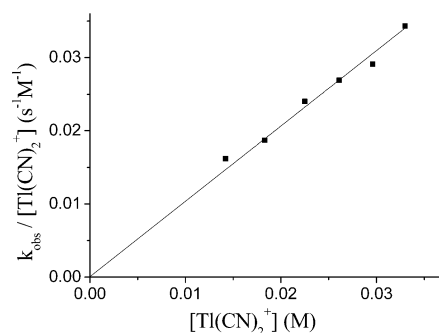
Results

Formation Kinetics of [(CN)₅Pt−Tl(CN)]⁻. Speciation in the Pt−Tl−CN⁻ system exhibits composite features, as more than one metal−metal bonded complex may coexist in the solution depending on the concentrations and concentration ratios of the metal ions and the ligand. Nevertheless, specific conditions can be designed where the predominant species is the [(CN)₅Pt−Tl(CN)]⁻ complex and the kinetics of reaction 1 can conveniently be studied (Figure 2).
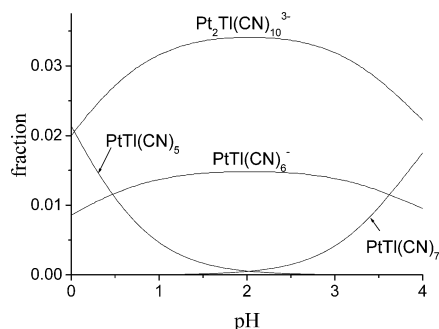
Preliminary experiments showed that the formation of [(CN)₅Pt−Tl(CN)]⁻ is relatively slow and could be followed by the standard mix-and-measure spectrophotometric technique. Rate constants, obtained under pseudo-first-order conditions ($[Tl(CN)_2^+] \gg [Pt(CN)_4^{2-}]$) at different wavelengths agreed within the experimental error. Single-exponential kinetic traces indicate that the reaction is first-order for the $[Pt(CN)_4^{2-}]$ reactant. The pseudo-first-order rate constants, k_{obs} (see Table S1), show second-order $[Tl(CN)_2^+]$ dependence (Figure 3), were found to be independent of both [HCN] and [CN⁻] concentrations, and can be written in the following form:

$$k_{obs} = (k_1[Tl(CN)_2^+] + k_{-1})[Tl(CN)_2^+] \qquad (3)$$

where k_1 and k_{-1} are the forward and the reverse rate constants for reaction 1. The almost zero intercept (small

(14) Microcal Origin 6.1 curve fitting program, OriginLab Corporation.
(15) MicroMath Scientist data fitting program, MicroMath Scientific Software, Inc.

Figure 3. $k_{obs}/[Tl(CN)_2^+]$ vs $[Tl(CN)_2^+]$ plot at $[Pt(CN)_4^{2-}]_{tot} = 0.0025$ M; $[Tl^{3+}]_{tot} = 0.020-0.045$ M; $[CN^-]_{tot} = 2.5[Tl^{3+}]_{tot}$ and pH = 1.90.


Figure 4. Typical concentration distribution of the Tl containing species in aqueous solution as a function of pH. The calculations were made with stability constants taken from ref 3. $[Pt(CN)_4]^{2-} = 0.10$ M, $[Tl^{3+}]_{tot} = 0.0050$ M, and $[CN^-]_{tot} = 0.0142$ M.

value of k_{-1}) of the appropriate plot of $k_{obs}/[Tl(CN)_2^+]$ versus $[Tl(CN)_2^+]$ (Figure 3) is in agreement with the large equilibrium constant reported for the formation of [(CN)₅Pt−Tl(CN)]⁻ (log $K_1 = 4.2$).[3] Therefore, direct experimental information could not be obtained for k_{-1} and its value could only be calculated as $k_{-1} = k_1/K_1$. The fitted value of $k_1 = 1.04 \pm 0.02$ M⁻² s⁻¹ and $k_{-1} = k_1/K_1 = 7 \times 10^{-5}$ M⁻¹ s⁻¹.

Formation Kinetics of [(CN)₅Pt−Tl−Pt(CN)₅]³⁻. As discussed in the introduction part, a trinuclear complex, [(NC)₅Pt−Tl−Pt(CN)₅]³⁻, can form Pt/Tl ratio larger than 1 (Figure 4). The reaction was followed in the 290−360 nm region. A large excess of $[Pt(CN)_4^{2-}]$ was used over $[Tl(CN)_2^+]$ to shift the equilibria to the formation of the [(NC)₅Pt−Tl−Pt(CN)₅]³⁻ complex and to maintain pseudo-first-order conditions. When the reaction was triggered by mixing $Pt(CN)_4^{2-}$ and $Tl(CN)_2^+$ in appropriate amounts, complex kinetic patterns were observed which featured an induction period (see Figure 5). This indicates that the [(NC)₅Pt−Tl−Pt(CN)₅]³⁻ complex is formed in a composite kinetic process presumably via the [(CN)₅Pt−Tl(CN)]⁻ intermediate. Such complications were not observed and single-exponential kinetic curves were recorded when $Pt(CN)_4^{2-}$ was reacted with the [(CN)₅Pt−Tl(CN)⁻] complex. This finding corroborates the assumption that the latter species acts as a precursor in the formation of [(NC)₅Pt−Tl−Pt(CN)₅]³⁻ when the reactants are $Pt(CN)_4^{2-}$ and Tl-$(CN)_2^+$. Detailed kinetic studies of reaction 2b were made with [(CN)₅Pt−Tl(CN)⁻] solutions which were allowed to reach chemical equilibrium overnight. Single-exponential kinetic traces and the linear dependence of k_{obs} versus $[Pt(CN)_4^{2-}]$ (Figure 6) and [HCN] (Figure 7) clearly confirm
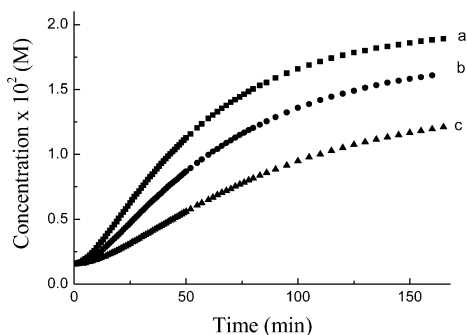
Figure 5. Formation kinetics of the complex $[(NC)_5Pt-Tl-Pt(CN)_5]^{3-}$ in aqueous solution at pH = 3.0. Data sets represent concentrations of the starting $[Pt(CN)_4]^{2-}$ and $[Tl(CN)_2(aq)]^+$ complexes: 0.13 and 0.02 M (a), 0.10 and 0.02 M (b), 0.10 and 0.016 M (c).
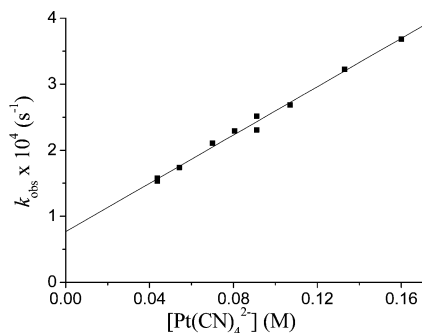
Figure 6. k_{obs} vs $[Pt(CN)_4{}^{2-}]$ plot with $[(CN)_5Pt-Tl(CN)^-] = 0.0041$ M ($[Tl^{3+}]_{tot} = 0.0050$, $[CN^-]_{tot} = 0.0142$ M) and pH = 1.90; $[Pt(CN)_4{}^{2-}]_{tot} = 0.050-0.17$ M.
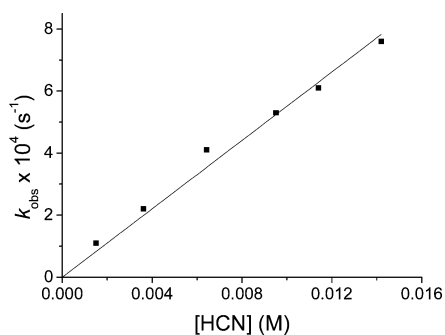
Figure 7. k_{obs} vs [HCN] plot at constant $[Pt(CN)_4{}^{2-}]_{tot} = 0.0909$ M ($[Pt(CN)_4{}^{2-}] = 0.0854$ M); $[Tl^{3+}]_{tot} = 0.0033$ M; $[(CN)_5Pt-Tl(CN)^-] = 0.00102$ M and $[CN^-] = 2.8 \times 10^{-10}$ M; and with different $[CN^-]_{tot} = 0.00807-0.0207$ M ([HCN] 0.0015−0.0142 M) and pH = 1.34−2.20.

that the reaction is first-order in both reactants and HCN catalyzes the reaction. Under these conditions the concentration of the individual species cannot be changed independently. We made several attempts to test how other components may affect the reaction, but the rate was found to be independent of the concentrations of other species (i.e., CN^-, $Tl(CN)_2{}^+$, and pH). Thus, the pseudo-first-order rate constant can be written in the following form:

$$k_{obs} = (k_{2b}[Pt(CN)_4{}^{2-}] + k_{-2b})[HCN] \qquad (4)$$

where k_{2b} and k_{-2b} are the forward and the reverse rate constants for reaction 2b. The $[Pt(CN)_4{}^{2-}]$ and [HCN] dependent experimental rate constants were fitted simultaneously on the basis of eq 4 by replacing the reverse rate constant with $k_{-2b} = k_{2b}/K_{2b}$. The fitted values are $k_{2b} = 0.45$

$\pm\ 0.04\ M^{-2}\ s^{-1}$, $K_{2b} = 26 \pm 6\ M^{-1}$, $k_{-2b} = k_{2b}/K_{2b} = 0.017$ $M^{-1}\ s^{-1}$ (see Table S1). The stability constant of the trinuclear complex is in excellent agreement with the result obtained independently (25 M^{-1}) using ^{205}Tl and ^{195}Pt NMR measurements.[3]

Discussion

The Formation of the $[(CN)_5Pt-Tl(CN)]^-$ Complex. According to NMR and EXAFS results on the binuclear Pt−Tl cyanide complex in aqueous solution, both platinum and thallium have octahedral geometries in this complex (i.e., four water molecules coordinate to the thallium center in the Pt−Tl cluster and also in $Tl(CN)_2{}^+$).[2,5] The stoichiometry of reaction 1 requires that, apart from the formation of the metal−metal bond, the Tl center releases one cyanide ion and the coordination number of Pt increases from four to six during the complex formation. Therefore any kinetic model for this reaction needs to include a metal−metal bond formation step and should also account for the transfer of a cyanide ion from the Tl to the Pt center.

In principle, simple first-order dependence on $[Pt(CN)_4{}^{2-}]$ and $[Tl(CN)_2{}^+]$ would be plausible as such a rate law could account for the formation of the Pt−Tl bond and the stoichiometry of the reaction. However, the overall order of the rate law is three, strongly resembling the rate law found[8] for the formation of the $[(CN)_5Pt-Tl(CN)_3]^{3-}$ complex. It follows that a reaction path through a cyanide bridged intermediate, which would imply an intramolecular rearrangement step, can be rejected similarly to the formation of the $[(CN)_5Pt-Tl(CN)_3]^{3-}$ complex.[8] In that case, the mechanism postulated the coordination of a fifth cyanide ligand from the bulk to the platinum center. It was assumed that the product is stabilized by the release of another cyanide from the thallium side. Provided that the formation of the $[(CN)_5-Pt-Tl(CN)]^-$ complex occurs in a similar fashion, a cyanide source is necessary to form the corresponding axially coordinated Pt center. In acidic solution CN^- is present at extremely low concentration levels and a direct reaction with this species can be excluded. The two major CN^- containing species are $[Tl(CN)_2]^+$ and HCN, and they were present in comparable concentrations in our experiments. However, k_{obs} was independent of the concentration of HCN, confirming that the cyanide is not coming from the bulk HCN, i.e., this species cannot be the source of the axial ligand. On the other hand, the second-order dependence of k_{obs} on $[Tl(CN)_2{}^+]$ directly indicates that this complex donates the fifth cyanide to the Pt center.

The ability of Tl(III) to adopt different compositions and geometries has been discussed elsewhere.[8] The structure of the thallium halide and pseudohalide complexes was studied both in the solid state and in solution by means of IR, Raman,[16−18] X-ray diffraction,[19−25] and ^{205}Tl NMR spectro-

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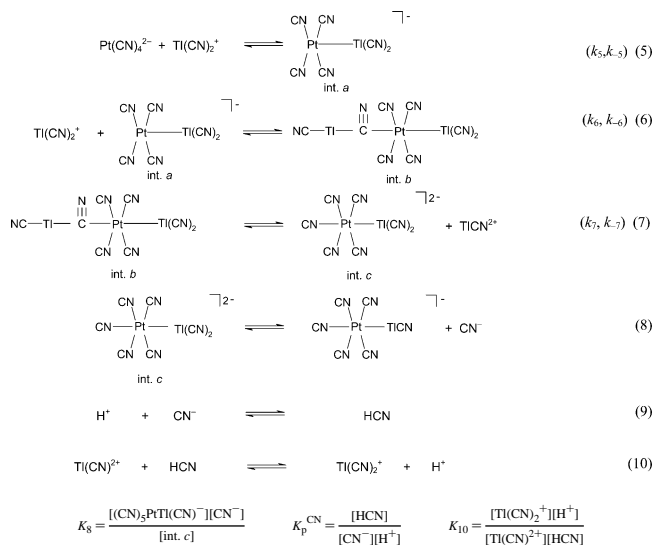(17) Carr, C. Ph.D. Thesis, University of Bristol, England, 1984.
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scopy.[10,26] Detailed studies of the ligand exchange reactions of the parent $Tl(CN)_n^{3-n}$ complexes[27,28] have concluded that "self-exchange" reactions (i.e., a direct encounter of two thallium(III) cyano complexes) play a dominant role besides the anation and the ligand substitution reactions. The dominance of the "self-exchange" reactions, especially in systems with ligand/metal ratio <6, is the consequence of low cyanide ion concentration and the low reactivity of HCN. These observations support the assumption that $Tl(CN)_2^+$ donates the "extra" cyanide.

The following model is consistent with the experimental observations (of eq 3):

$$(k_5, k_{-5}) \quad (5)$$

$$(k_6, k_{-6}) \quad (6)$$

$$(k_7, k_{-7}) \quad (7)$$

$$(8)$$

$$H^+ + CN^- \rightleftharpoons HCN \quad (9)$$

$$Tl(CN)^{2+} + HCN \rightleftharpoons Tl(CN)_2^+ + H^+ \quad (10)$$

$$K_8 = \frac{[(CN)_5PtTl(CN)^-][CN^-]}{[int.\ c]} \qquad K_p^{CN} = \frac{[HCN]}{[CN^-][H^+]} \qquad K_{10} = \frac{[Tl(CN)_2^+][H^+]}{[Tl(CN)^{2+}][HCN]}$$
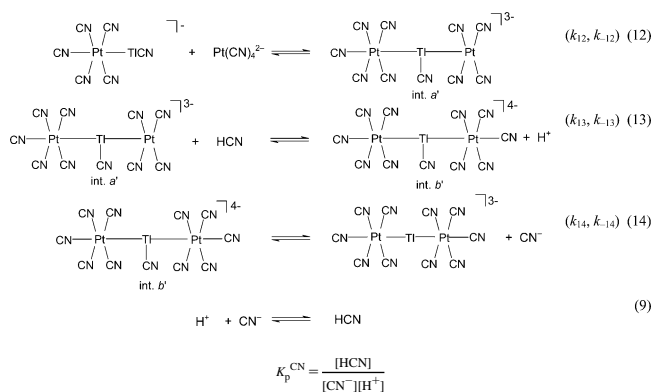
Assuming that intermediates a and b are in the steady state and reactions $8-10$ are fast equilibria, standard derivation yields the following expression for k_1 and k_{-1}:

$$k_1 = \frac{k_5 k_6 k_7}{k_{-5}k_{-6} + k_{-5}k_7 + k_6 k_7[Tl(CN)_2^+]}$$

$$k_{-1} = \frac{\dfrac{k_{-5}k_{-6}k_{-7}}{K_8 K_p^{CN} K_{10}}}{k_{-5}k_{-6} + k_{-5}k_7 + k_6 k_7[Tl(CN)_2^+]} \quad (11)$$

The first $Tl(CN)_2^+$ can coordinate to the platinum center via the thallium ion (eq 5; formation of a partial metal–metal bond in a dominantly electron transfer step), or via one of its cyanide ligands (forming a cyano-bridged Tl–

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$\mu CN \cdots Pt(CN)_4$ entity). Thus the sequence of the metal–metal bond formation and the coordination of the fifth cyanide to Pt(II) can be reversed. The experimental observations do not allow us to make a distinction between these alternatives, in analogy with $[(CN)_5Pt–Tl(CN)_3]^{3-}$ formation.[8] Whatever the order of the first two steps is, the cyano-bridged $Tl(CN)^{2+}$ has to be released and the (N)C–Pt–Tl entity with a strong axial bond of the Pt center is formed after the formation of the trinuclear intermediate b.[7] (The break of the Tl–μCN bond, the tight coordination of the axial cyanide to Pt, and the shortening of the Pt–Tl bond is unlikely an elementary step, but we have no information about the intimate details.) In fact the product of eq 7, i.e., $[(CN)_5Pt–Tl(CN)_2]^{2-}$, is a "ready" metal–metal bonded complex, which can be converted to the $[(CN)_5Pt–Tl(CN)]^-$ complex in the fast reaction 8.[3] Reactions 9 and 10 are also known to be fast steps.[29] Equation 11 predicts that eventually $Tl(CN)_2^+$ should inhibit the overall reaction. Because of experimental constraints, such a concentration dependence could not be confirmed.

The Formation of the $[(CN)_5Pt–Tl–Pt(CN)_5]^{3-}$ Complex. This species is also formed in an overall third-order process from $[(CN)_5Pt–Tl(CN)]^-$ and $Pt(CN)_4^{2-}$. As in the previous case, formally these complexes can be combined into the trinuclear complex and the stoichiometry of the corresponding reaction would not require the involvement of HCN. The kinetic role of HCN can be understood in terms of a mechanism which includes the metal–metal bond formation and axial coordination of a cyanide to the Pt center. In this case, experiments were run under conditions where HCN was present in orders of magnitude higher concentrations than the cyanide donors identified in the other reactions, i.e., in the formation of the $[(CN)_5Pt–Tl(CN)_3]^{3-}$ and the $[(CN)_5Pt–Tl(CN)]^-$ complexes. Thus, in agreement with the experimental results (eq 4), it needs to be concluded that HCN donates the fifth Pt–cyanide in this reaction. The proposed model for the formation of the trinuclear complex is as follows:

$$(k_{12}, k_{-12}) \quad (12)$$

$$(k_{13}, k_{-13}) \quad (13)$$

$$(k_{14}, k_{-14}) \quad (14)$$

$$H^+ + CN^- \rightleftharpoons HCN \quad (9)$$

$$K_p^{CN} = \frac{[HCN]}{[CN^-][H^+]}$$

The following expression can be derived for k_{2b} and k_{-2b} by assuming that intermediates a' and b' are in the steady

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state and reaction 9 is a fast equilibrium:

$$k_{2b} = \frac{k_{12}k_{13}k_{14}}{k_{-12}k_{-13}[H^+] + k_{-12}k_{14} + k_{13}k_{14}[HCN]}$$

$$k_{-2b} = \frac{\dfrac{k_{-12}k_{-13}k_{-14}}{K_p^{CN}}}{k_{-12}k_{-13}[H^+] + k_{-12}k_{14} + k_{13}k_{14}[HCN]} \quad (15)$$

If reaction 13 is the rate determining step (as it is in case of the formation of the binuclear complexes[8]) and therefore $k_{-12}k_{14} \gg k_{-12}k_{-13}[H^+] + k_{13}k_{14}[HCN]$, this expression can be simplified, i.e., $k_{2b} = k_{12}k_{13}/k_{-12}$ and $k_{-2b} = k_{-13}k_{-14}/(k_{14}K_p)$. Data fitting is in agreement with this assumption as the fitted and observed k_{obs} values show less than 10% deviations (Table S1).

In the formation of the binuclear species, the order of the metal−metal bond formation and the coordination of the fifth cyanide ion to the Pt center could not be elaborated and the alternative models provided equivalent interpretation of the experimental results. Such an ambiguity does not exist when the formation of $[(CN)_5Pt-Tl-Pt(CN)_5]^{3-}$ is considered. Reversing the order of steps 12 and 13 would predict proton inhibited complex formation. Such a pH effect was not observed experimentally confirming that the alternative model is not feasible. The fact that the ligand exchange between free HCN and $Pt(CN)_4^{2-}$ is unmeasurably slow strongly supports our assumption.[30,31]

Summary

The results presented here confirm that Pt−Tl bonded cyano complexes are formed via very similar reaction paths. The overall reaction includes (i) metal−metal bond formation and (ii) the coordination of a fifth cyanide ion to Pt. The order of these two steps was undoubtedly established in the formation of $[(CN)_5Pt-Tl-Pt(CN)_5]^{3-}$. It is most likely that the same sequence is valid in the formation of $[(CN)_5Pt-Tl(CN)]^-$ and $[(CN)_5Pt-Tl(CN)_3]^{3-}$, i.e., the metal−metal bond formation is the first step. It is a partial electron transfer reaction which reduces the electron density of, and enhances nucleophilic attack at, the Pt center. The corresponding reactions are different in the nucleophilic agent which donates the fifth cyanide to Pt.

In the alkaline to slightly acidic pH range CN^- catalyzes the formation of the $[(CN)_5Pt-Tl(CN)_3]^{3-}$ and HCN has negligible effect even when it is present at considerably higher concentrations than CN^-. This difference in the kinetic behavior is in line with the fact that CN^- is a much stronger nucleophile than HCN and strongly suggests that step ii is a nucleophilic addition.

The concentration of CN^- is very low at pH ∼2 and Tl$(CN)_2^+$ is the nucleophilic agent in the formation of $[(CN)_5Pt-Tl(CN)]^-$. Although HCN is present at comparable concentrations to Tl$(CN)_2^+$, it does not affect the complex formation kinetics. To some extent it is surprising that Tl$(CN)_2^+$ is more reactive (virtually it is a stronger nucleophile) than HCN. The noted difference can be understood by considering that the attractive electrostatic interactions between the negatively charged intermediate *a* and the positively charged Tl$(CN)_2^+$ promote reaction 6. Such an enhancement is absent with HCN.

Finally, the results for the formation of the trinuclear complex confirm that HCN can also act as a nucleophilic agent and donate a cyanide ligand to the Pt center. In this case, other nucleophiles are present at very low concentration levels and the reaction occurs with HCN simply because it is present in sufficiently large concentration.

In light of the results presented here, further studies should address how various ligands coordinated to the Tl(III) center and the presence of other nucleophiles affect the formation kinetics of Pt−Tl bonded complexes. Detailed studies toward this direction are under way in our laboratories.

Supporting Information Available: Table of concentrations, observed and calculated k_{obs} values, and their deviations and derivation of the rate expressions on the basis of the models. This material is available free of charge via the Internet at http://pubs.acs.org.

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