

Kinetics and Mechanism of Formation of the Platinum–Thallium Bond:
The $[(\text{CN})_5\text{Pt}-\text{Tl}(\text{CN})_3]^{3-}$ ComplexPéter Nagy,[†] Imre Tóth,^{*,†} István Fábián,[†] Mikhail Maliarik,[‡] and Julius Glaser[§]

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Received June 16, 2003

Formation kinetics of the metal–metal bonded $[(\text{CN})_5\text{PtTi}(\text{CN})_3]^{3-}$ complex from $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Tl}(\text{CN})_4^-$ has been studied in the pH range of 5–10, using standard mix-and-measure spectrophotometric technique at pH 5–8 and stopped-flow method at pH > 8. The overall order of the reaction, $\text{Pt}(\text{CN})_4^{2-} + \text{Tl}(\text{CN})_4^- \rightleftharpoons [(\text{CN})_5\text{PtTi}(\text{CN})_3]^{3-}$, is 2 in the slightly acidic region and 3 in the alkaline region, which means first order for the two reactants in both cases and also for CN^- at high pH. The two-term rate law corresponds to two different pathways via the $\text{Tl}(\text{CN})_3$ and $\text{Tl}(\text{CN})_4^-$ complexes in acidic and alkaline solution, respectively. The two complexes are in fast equilibrium, and their actual concentration ratio is controlled by the concentration of free cyanide ion. The following expression was derived for the pseudo-first-order rate constant of the overall reaction: $k_{\text{obs}} = (k_1^a[\text{Tl}(\text{CN})_4^- + (k_1^a/K_f)]/(1 + K_p[\text{H}^+]))[\text{CN}^-]_{\text{free}} + k_1^b[\text{Tl}(\text{CN})_4^-] + (k_1^b/K_f)$, where k_1^a and k_1^b are the forward rate constants for the alkaline and slightly acidic paths, K_f is the stability constant of $[(\text{CN})_5\text{PtTi}(\text{CN})_3]^{3-}$, and K_p is the protonation constant of cyanide ion. $k_1^a = 143 \pm 13 \text{ M}^{-2} \text{ s}^{-1}$, $k_1^b = 0.056 \pm 0.004 \text{ M}^{-1} \text{ s}^{-1}$, $K_f = 250 \pm 54 \text{ M}^{-1}$, and $\log K_p = 9.15 \pm 0.05$ ($I = 1 \text{ M NaClO}_4$, $T = 298 \text{ K}$). Two possible mechanisms were postulated for the overall reaction in both pH regions, which include a metal–metal bond formation step and the coordination of the axial cyanide ion to the platinum center. The alternative mechanisms are different in the sequence of these steps.

Introduction

The chemistry of metal–metal bonded compounds has generated substantial interest during the last two decades.^{1,2} Important properties of these complexes range from catalytic activity³ through unusual magnetic or optical properties⁴ to their application as precursors in synthesis.⁵ Recently, we have reported the synthesis and structural features of four binuclear platinum–thallium cyano compounds containing

a direct and unsupported by ligands metal–metal bond. The complexes, prepared in a direct reaction between $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Tl}(\text{CN})_n^{3-n}$ in aqueous solution, were found to be surprisingly stable under certain conditions despite the strong oxidative properties of thallium(III).^{6,7} The structure of the products is represented by the formula $[(\text{CN})_5\text{Pt}-\text{Tl}(\text{CN})_n]^{m-}$ ($n = 0-3$) as determined by means of multinuclear NMR (¹⁹⁵Pt, ²⁰⁵Tl, ¹³C) and supported by Raman spectroscopy. In addition, a trinuclear complex with the formula $[(\text{CN})_5\text{Pt}-\text{Tl}-\text{Pt}(\text{CN})_5]^{3-}$ has been prepared in aqueous solution via reversible reactions.⁶⁻⁸ Extended X-ray absorption fine structure studies of the complexes confirmed short Pt–Tl bond lengths (2.60–2.63 Å) in both solution and solid phase and also allowed the establishment of the presence of water

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molecules, which are coordinated to the thallium center together with cyanide ligands and a platinum atom.^{9,10} Several analogues of $[(\text{NC})_5\text{Pt}-\text{Tl}(\text{CN})_n]^{m-}$, in which the cyanides are replaced by different ligands (en, dipy, nta, edta, dmsO) at the Tl center, have been prepared and characterized in solid phase by X-ray spectroscopy.^{11–13} The $(\text{NC})_5\text{Pt}-\text{Tl}$ unit is present in all complexes with short (about 2.6 Å) bonds between Pt–Tl in the linear NC–Pt–Tl entity. The unusually strong metal–metal bond has induced detailed computational studies on the electronic structure of these complexes.^{14,15} In this work, we present our first insight into the kinetics and mechanism of the formation of these novel metal–metal bonded complexes. The formation kinetics of the $[(\text{NC})_5\text{Pt}-\text{Tl}(\text{CN})_3]^{3-}$ complex, a member of the Pt–Tl cyanides, was followed by using spectrophotometric methods.

Experimental Section

Materials. A concentrated (1.204 M) aqueous solution of $\text{Tl}(\text{ClO}_4)_3$ in 4.95 M HClO_4 was obtained by anodic oxidation of TlClO_4 .¹⁶ The thallium(III) concentration was determined by bromatometric titration. Solutions of thallium(III) cyanide complexes were synthesized by addition of a calculated volume of a sodium cyanide solution (and NaOH when needed) to the stock solution of thallium(III) perchlorate.¹⁷ The solution of sodium tetracyanoplatinate(II) was prepared either by precipitation of potassium perchlorate from the aqueous solution of $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ (Aldrich, reagent grade) with an excess of aqueous sodium perchlorate or by dissolution of solid $\text{Pt}(\text{CN})_2$ (Aldrich, reagent grade) in water by addition of 2 equiv of NaCN. The dissolution took about 2 h under vigorous stirring. The solutions contained 1 M NaClO_4 as ionic medium and were kept in the dark to avoid photochemical decomposition.¹⁸

pH Measurements. pH values were measured by a combination electrode (Metrohm, 6.0234.100) connected to a pH meter (Radiometer PHM26). The pH meter was calibrated using the method of Irving et al.¹⁹ The pH corresponds to $-\log[\text{H}^+]$ through this paper.

NMR Measurements. ¹⁹⁵Pt NMR spectra were recorded with a Bruker AM400 spectrometer, ¹³C spectra with a Bruker AM360 spectrometer at a probe temperature of 298 (±0.5) K. Typical NMR parameters for obtaining ¹⁹⁵Pt and ¹³C spectra were presented in our recent publications.^{7,8} The chemical shifts (ppm) were referred toward higher frequency from signals of aqueous 0.1 M Na_2PtCl_6 (4533 ppm to higher frequency from $\Xi(^{195}\text{Pt}) = 21.4$ MHz at 25 °C) and water-soluble sodium salt of TMS, for ¹⁹⁵Pt and ¹³C NMR spectra, respectively.

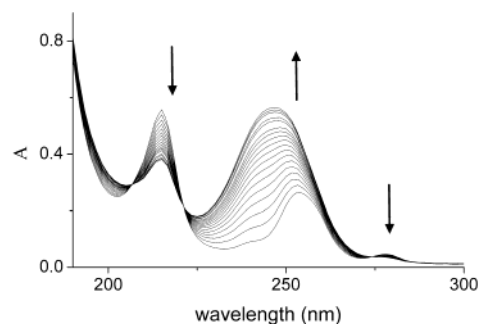


Figure 1. Spectral changes as function of time during the formation of the $[(\text{CN})_5\text{Pt}-\text{Tl}(\text{CN})_3]^{3-}$ complex (duration of the experiment 55 min): 0.25 mM $[\text{Pt}(\text{CN})_4]^{2-}$; pH = 5.15; $[\text{CN}^-]_{\text{tot}} = 96$ mM; $[\text{Ti}^{3+}]_{\text{tot}} = 9$ mM initial concentrations; $l = 1$ mm.

Kinetic Measurements. UV–vis spectrophotometry is suitable to follow the complex formation reaction because the $\text{Pt}(\text{CN})_4^{2-}$ and the $[(\text{CN})_5\text{Pt}-\text{Tl}(\text{CN})_3]^{3-}$ complexes have distinguishing absorption bands in the wavelength range 200–280 nm (Figure 1). Because of the strong molar absorbance of these species ($\sim 10^4$ $\text{M}^{-1} \text{cm}^{-1}$) and relatively low Pt concentration (typically 0.25 mM), thin optical cells had to be used in the spectrophotometric measurements. At pH < 8, kinetic data were collected with a CARY 1E UV–vis spectrophotometer, using 1, 0.1, 0.02, and 0.001 cm wide optical cells. At pH > 8, the stopped-flow measurements were made with an Applied Photophysics DX-17 MV instrument at 278 nm using a 1 cm optical path. Temperature was set to 298 K in all cases. The stability constant of the $[(\text{CN})_5\text{Pt}-\text{Tl}(\text{CN})_3]^{3-}$ complex is $K_f = 200 \text{ M}^{-1}$,⁸ therefore a large excess of $[\text{Ti}(\text{CN})_4^-]$ had to be used to maintain relatively high conversions. The kinetic curves were fitted with an Origin (Microcal) routine,²⁰ and all experimental rate constants were evaluated simultaneously with Scientist (MicroMath) data analysis program.²¹

Concentration Ranges. a. pH = 8–10 Region. $[\text{Ti}(\text{CN})_4^-]$ dependence: $[\text{Ti}(\text{CN})_4^-]_{\text{tot}} = 0.003\text{--}0.011$ M; with constant 0.25 mM $[\text{Pt}(\text{CN})_4^{2-}]_{\text{tot}}$, $[\text{CN}^-] = 0.0269$ M, and pH = 8.91. $[\text{CN}^-]$ dependence: $[\text{CN}^-] = 0.019\text{--}0.052$ M; with constant 0.25 mM $[\text{Pt}(\text{CN})_4^{2-}]_{\text{tot}}$, 9 mM $[\text{Ti}(\text{CN})_4^-]_{\text{tot}}$, and pH = 8.91. pH dependence: pH = 8–10; with constant 0.25 mM $[\text{Pt}(\text{CN})_4^{2-}]_{\text{tot}}$, 9 mM $[\text{Ti}^{3+}]_{\text{tot}}$, and 96 mM $[\text{CN}^-]_{\text{tot}}$.

b. pH = 5–8 Region. $[\text{Ti}(\text{CN})_4^-]$ dependence: $[\text{Ti}(\text{CN})_4^-]_{\text{tot}} = 0.003\text{--}0.011$ M; with constant 0.25 mM $[\text{Pt}(\text{CN})_4^{2-}]_{\text{tot}}$, $[\text{CN}^-] = 8.48 \cdot 10^{-6}$ M, and pH = 5.15. $[\text{CN}^-]$ dependence: $[\text{CN}^-] = 5.6 \cdot 10^{-6}\text{--}1.5 \cdot 10^{-5}$ M; with constant 0.25 mM $[\text{Pt}(\text{CN})_4^{2-}]_{\text{tot}}$, 10 mM $[\text{Ti}(\text{CN})_4^-]_{\text{tot}}$, and pH = 5.15. pH dependence: pH = 4.8–7.8; with constant 0.25 mM $[\text{Pt}(\text{CN})_4^{2-}]_{\text{tot}}$, 9 mM $[\text{Ti}^{3+}]_{\text{tot}}$, 96 mM $[\text{CN}^-]_{\text{tot}}$, and 90 mM hepes ($\text{C}_8\text{H}_{18}\text{N}_2\text{O}_4\text{S}$) as a buffer.²²

Results

Our previous studies on the $\text{Pt}(\text{CN})_4^{2-}-\text{Ti}^{3+}-\text{CN}^--\text{H}_2\text{O}$ system allowed us to detect and characterize thoroughly a number of di- and trinuclear metal–metal bonded complexes. Although the speciation in solution is typically complex, the concentrations of the individual species can be adjusted relatively easily by selecting appropriate experimental condi-

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 (22) In the following text, square brackets, [], are consequently 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.

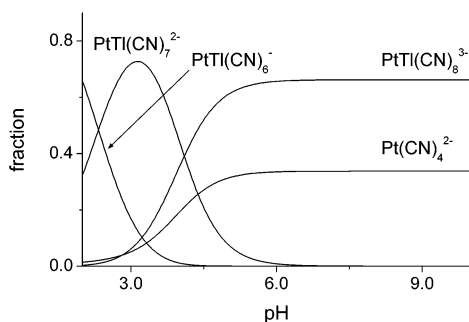
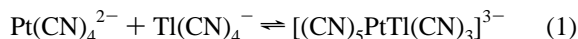


Figure 2. Typical concentration distribution of the Pt-containing species in aqueous solution as a function of pH based on the stability constants of the complexes from ref 8. Conditions: 0.25 mM $[\text{Pt}(\text{CN})_4^{2-}]$, 10 mM $[\text{Tl}^{3+}]_{\text{tot}}$, and 90 mM $[\text{CN}^-]_{\text{tot}}$.

tions. As demonstrated in Figure 2, the only Pt–Tl bonded complex is $[(\text{CN})_5\text{PtTi}(\text{CN})_3]^{3-}$ and the predominant form of thallium(III) is $\text{Tl}(\text{CN})_4^-$ when relatively high cyanide ion concentration is used at $\text{pH} \geq 5$. These conditions are appropriate for studying exclusively the formation kinetics of the $[(\text{CN})_5\text{PtTi}(\text{CN})_3]^{3-}$ complex without the interference of side-reactions:



$$K_f = \frac{[(\text{CN})_5\text{PtTi}(\text{CN})_3^{3-}]}{[\text{Pt}(\text{CN})_4^{2-}][\text{Tl}(\text{CN})_4^-]}$$

Time-resolved kinetic spectra show characteristic spectral changes in the UV region upon mixing solutions of $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Tl}(\text{CN})_4^-$ (Figure 1). According to preliminary experiments, the reaction is relatively slow at $\text{pH} = 5$ and could be studied by a standard mix-and-measure spectrophotometric technique. The reaction becomes excessively faster by increasing the pH, and eventually it can be monitored only by using the stopped-flow method. Spectrophotometric kinetic traces were evaluated in the 200–280 nm region at wavelengths where the spectra of $\text{Pt}(\text{CN})_4^{2-}$ and the bimetallic complex are sufficiently different and $\text{Tl}(\text{CN})_4^-$ has a relatively small contribution to the absorbance. Rate constants obtained under pseudo-first-order conditions ($[\text{Tl}(\text{CN})_4^-] \gg [\text{Pt}(\text{CN})_4^{2-}]$) at different wavelengths agreed within the experimental error. However, stopped-flow kinetic traces from the 200–270 nm region showed systematic deviations from the strictly exponential behavior at longer reaction times. This phenomenon was attributed to photochemical decomposition of the dinuclear species due to constant irradiation with the relatively high energy emission of the Xe lamp of the instrument, and the kinetic data were collected only at 278 nm, where $\text{Pt}(\text{CN})_4^{2-}$ is the dominant absorbing species.

Kinetic Studies in the $\text{pH} = 8$ –10 Region. Single-exponential kinetic traces and the linear dependence of k_{obs} on $[\text{Tl}(\text{CN})_4^-]$ clearly confirm that the reaction is first order in both reactants (Supporting Information (SI) Figure S1). The nonzero intercept of the appropriate plot of k_{obs} at constant $[\text{CN}^-]$ and pH allows independent determination of the forward and reverse rate constants of reaction 1: k_+

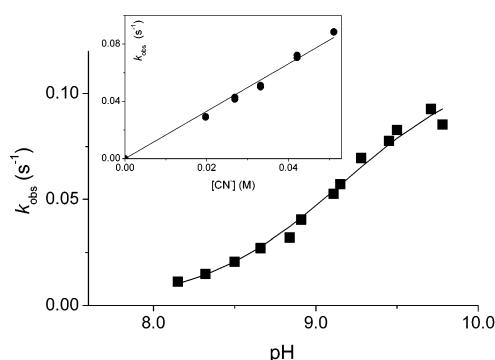


Figure 3. k_{obs} vs pH plot at 0.25 mM $[\text{Pt}(\text{CN})_4^{2-}]$, 9 mM $[\text{Tl}(\text{CN})_4^-]_{\text{tot}}$, and 96 mM $[\text{CN}^-]_{\text{tot}}$. Inset: k_{obs} vs $[\text{CN}^-]$ plot at 0.25 mM $[\text{Pt}(\text{CN})_4^{2-}]$, 9 mM $[\text{Tl}(\text{CN})_4^-]$, and $\text{pH} = 8.91$.

$= 3.0 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_- = 0.015 \pm 0.002 \text{ s}^{-1}$.²³ The ratio of the rate constants, $k_+/k_- = 200 \pm 24 \text{ M}^{-1}$, is in full agreement with $K_f = 200 \pm 28 \text{ M}^{-1}$, obtained in our previous study.⁸

The specific feature of this reaction is that it is also first order with respect to the cyanide ion, although CN^- itself is not involved in the stoichiometric equation for the formation of the bimetallic complex (eq 1). Because of experimental limitations, the cyanide concentration cannot be decreased without changing the speciation. Nevertheless, it can be shown that at constant pH and $[\text{Tl}(\text{CN})_4^-]$, k_{obs} is a linear function of $[\text{CN}^-]$ with zero intercept (Figure 3), indicating that the cyanide ion catalyzes the formation of the Pt–Tl species. Furthermore, the typical sigmoid pH profile of k_{obs} confirms that the deprotonated form of the ligand is more reactive than HCN (Figure 3). Provided that the concentration of $\text{Tl}(\text{CN})_4^-$ is constant and the protonation reaction of the cyanide ion is a fast equilibrium step compared to the formation of the bimetallic complex²⁴



k_{obs} can be expressed as

$$k_{\text{obs}} = (k_{\text{HCN}}K_p[\text{H}^+] + k_{\text{CN}^-}) \frac{1}{1 + K_p[\text{H}^+]} [\text{CN}^-]_{\text{free}} \quad (3)$$

where $K_p = [\text{HCN}]/[\text{CN}^-][\text{H}^+]$, $[\text{CN}^-]_{\text{free}} = [\text{HCN}] + [\text{CN}^-]$, and k_{CN^-} and k_{HCN} are the apparent rate constants for the reactions of the two forms of the ligand, respectively. Data fitting by use of a nonlinear least-squares routine yielded $k_{\text{CN}^-} = 1.26 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$ ($[\text{Pt}(\text{CN})_4^{2-}] = 0.25 \text{ mM}$, $[\text{Tl}(\text{CN})_4^-] = 9 \text{ mM}$) and $\log K_p = 9.2 \pm 0.1$, in reasonable agreement with 9.01 reported earlier.²⁵ These calculations also confirmed that the first term of eq 3 is negligible, $k_{\text{HCN}} = 0$, i.e., the HCN path has no measurable contribution to the overall reaction.

(23) k_+ and k_- stand for the apparent forward and reverse rate constants of reaction 1 throughout this paper and are dependent on the conditions applied.

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At pH = 8–10, the pH and concentration dependencies of k_{obs} are consistent with the expression

$$k_{\text{obs}} = (k_1^{\text{a}}[\text{Ti}(\text{CN})_4^-] + k_{-1}^{\text{a}}) \frac{1}{1 + K_{\text{p}}[\text{H}^+]} [\text{CN}^-]_{\text{free}} \quad (4)$$

where k_1^{a} and k_{-1}^{a} are the forward and reverse rate constants of reaction 1 at high pH.

Kinetic Studies in the pH = 5–8 Region. As expected, k_{obs} sharply decreases as the pH is decreased but the actual values are substantially higher than those predicted by eq 4. Under slightly acidic conditions (pH = 5.15), the predicted rate constant on the basis of eq 4 is already less than 5% of the experimental value. Under such conditions, k_{obs} is a linear function of $[\text{Ti}(\text{CN})_4^-]$ at constant free cyanide concentration (SI Figure S1) and the variation of $[\text{CN}^-]$ has a negligible effect on the reaction rate. The plot of k_{obs} as a function of $[\text{Ti}(\text{CN})_4^-]$ yields $k_+ = 0.057 \pm 0.005 \text{ M}^{-1} \text{ s}^{-1}$ and $k_- = (1.4 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$ (pH = 5.15, $[\text{Pt}(\text{CN})_4^{2-}] = 0.25 \text{ mM}$, and $[\text{CN}^-] = 8.5 \times 10^{-6} \text{ M}$).²⁶ These observations lead to the conclusion that another reaction path becomes operative in slightly acidic solution, and k_{obs} can be given by the expression

$$k_{\text{obs}} = k_1^{\text{b}}[\text{Ti}(\text{CN})_4^-] + k_{-1}^{\text{b}} \quad (5)$$

where k_1^{b} and k_{-1}^{b} are the forward and reverse rate constants for the reaction path in slightly acidic solution.

In the final evaluation, eqs 4 and 5 were combined and all experimental rate constants were fitted simultaneously on the basis of eq 6 by replacing the reverse rate constants with $k_{-1}^{\text{a}} = k_1^{\text{a}}/K_{\text{f}}$ and $k_{-1}^{\text{b}} = k_1^{\text{b}}/K_{\text{f}}$, respectively.

$$k_{\text{obs}} = \left(k_1^{\text{a}}[\text{Ti}(\text{CN})_4^-] + \frac{k_1^{\text{a}}}{K_{\text{f}}} \right) \frac{1}{1 + K_{\text{p}}[\text{H}^+]} [\text{CN}^-]_{\text{free}} + k_1^{\text{b}}[\text{Ti}(\text{CN})_4^-] + \frac{k_1^{\text{b}}}{K_{\text{f}}} \quad (6)$$

The fitted values are $k_1^{\text{a}} = 143 \pm 13 \text{ M}^{-2} \text{ s}^{-1}$, $k_1^{\text{b}} = 0.056 \pm 0.004 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{f}} = 250 \pm 54 \text{ M}^{-1}$, and $\log K_{\text{p}} = 9.15 \pm 0.05$.

The concentrations, the observed and calculated k_{obs} values, and their deviations are given in SI (Table S1).

Discussion

Although the formation of the $[(\text{CN})_5\text{Pt}-\text{Ti}(\text{CN})_3]^{3-}$ complex in reaction 1 does not require a change in the overall number of coordinated cyanide ions, there are substantial changes in the coordination spheres of the metal centers. In a recent structural study of the family of binuclear Pt–Tl cyanide complexes in aqueous solution, we found that the geometries in the $[(\text{CN})_5\text{Pt}-\text{Ti}(\text{CN})_3]^{3-}$ species are distorted

octahedral and tetrahedral for the platinum and thallium atoms, respectively,¹⁰ in contrast to the respective square-planar and tetrahedral geometries of the $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Ti}(\text{CN})_4^-$ precursor complexes. Thus, the formation of the metal–metal bond induces a geometric changeover from square planar to octahedral at the platinum center. It is clear from reaction 1 that, apart from the formation of a metal–metal bond, the Tl-center should release one cyanide ion and the coordination number of Pt should increase from four to six during the formation of the complex. It follows that 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. Furthermore, eq 4 implies the formation of a transient species with the $[\text{PtTi}(\text{CN})_9]^{4-}$ overall stoichiometry via the “alkaline” path.

The ability of Tl(III) to easily change its geometry, depending on the coordinated ligands, is well documented in the literature. Cyano complexes of thallium(III) are reasonably labile, and different routes for the ligand exchange reactions of the parent $\text{Ti}(\text{CN})_n^{+3-n}$ complexes were explored.^{27,28} According to these results, the cyanide exchange between $\text{Ti}(\text{CN})_4^-$ and the bulk cyanide (CN^- , HCN) proceeds via an I_{a} mechanism, i.e., via the formation of a pentacoordinated intermediate. This reaction is much faster ($k_{\text{ij}} = 9.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) than the formation of the bimetallic complex. Thallium(III) is also known to adopt different geometries in its halide and pseudohalide complexes. For example, the $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ and $\text{TlX}_n(\text{H}_2\text{O})_{6-n}^{(3-n)+}$ complexes ($X = \text{halide, cyanide, } n = 1, 2$) are octahedral while TlX_4^- is tetrahedral.²⁹ The energy difference between the possible conformational isomers seems to be very small in the case of $\text{TlX}_3(\text{H}_2\text{O})_x$ complexes, and even the hydration numbers in these species are somewhat uncertain in aqueous solution. The bulkiness of the ligand may be a key factor in affecting the stability of the possible isomers.^{30,31}

The dynamic behavior of the ligands in the Pt–Tl-cyano complex also merits consideration in order to elaborate a plausible kinetic model. The labilities of the cyanide ligands in various positions of the bimetallic species are very different. The two CN sites (axial and equatorial) at the Pt center are quite inert in the $[(\text{CN})_5\text{Pt}-\text{Ti}(\text{CN})_3]^{3-}$ complex as well as in other species of the $[(\text{CN})_5\text{Pt}-\text{Ti}(\text{CN})_n]^{n-}$ family. Selectively ¹³C-enriched compounds at the equatorial Pt-sites could be prepared in acidic solution.⁷ This implies that the equatorial cyanides cannot be involved in any intramolecular rearrangement of the intermediate(s) formed in the overall reaction. Different routes for the ligand exchange reactions of the parent $\text{Ti}(\text{CN})_n^{3-n}$ complexes are

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(26) The ratio of the rate constants, $k_+/k_- = 410 \pm 120 \text{ M}^{-1}$. This value is about two times higher than the stability constant of the complex (reaction 1). However, this seems to still be in an acceptable agreement taking into account the experimental limitations, i.e., the limited applicable concentration ranges and the difficulties with controlling the pH in an unbuffered solution.

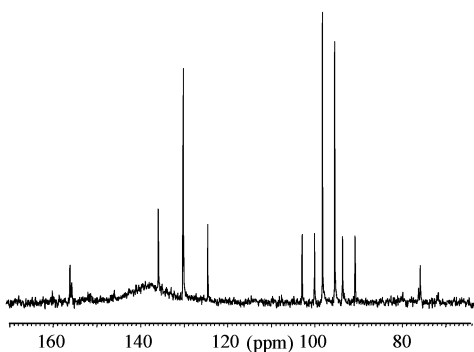
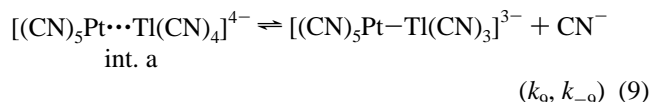
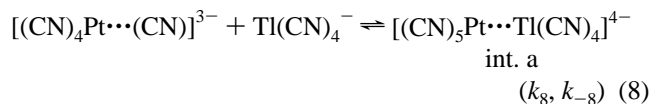
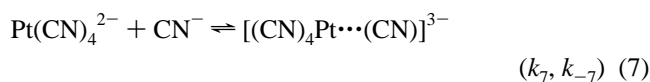


Figure 4. A typical 90-MHz ^{13}C NMR spectrum of the $[(^{13}\text{C})(^{12}\text{C})_4\text{Pt}-\text{Tl}(^{13}\text{C})_3]^{3-}$ species recorded at $\text{pH} \approx 9$ with 30 mM $[\text{Tl}^{3+}]_{\text{tot}}$, 180 mM Na^{13}CN , and 30 mM $\text{Pt}(^{12}\text{CN})_4^{2-}$. The narrow signals ($\Delta\gamma_{1/2} < 10$ Hz) belong to the cyano ligands coordinated to Pt in the metal–metal bonded complex centered at 97 ppm (^{13}C : $^2J_{\text{Tl}-\text{C}} = 255$ Hz, $^1J_{\text{Pt}-\text{C}} = 843$ Hz) and 116 ppm (^{13}C : $^1J_{\text{Tl}-\text{C}} = 7270$ Hz, $^1J_{\text{Pt}-\text{C}} = 742$ Hz, hardly visible) and to the $\text{Pt}(\text{CN})_4^{2-}$ species (centered at 130 ppm, $^1J_{\text{Pt}-\text{C}} = 1031$ Hz). Time-averaged broad signal ($\Delta\gamma_{1/2} > 300$ Hz) at around 135 ppm is from the labile CN ligands coordinated to the thallium site of the bimetallic complex and $\text{Tl}(\text{CN})_4^-$, together with the free cyanides.

known.^{27,28} At high pH, the exchange between the CN ligands coordinated to the thallium center and the bulk is much faster compared to the formation rate of the complex. Similar or even faster exchange rate is expected for the Tl–CN ligands in the Pt–Tl bonded intermediates and complexes. In other words, the CN^- ligands can easily leave the Tl sites and act as nucleophilic agents at the axial position of Pt. A typical ^{13}C NMR spectrum of the Pt–Tl complex (Figure 4) recorded at $\text{pH} \approx 9$ shows clearly the different labilities of the ligands in the $[(^{13}\text{C})(^{12}\text{C})_4\text{Pt}-\text{Tl}(^{13}\text{C})_3]^{3-}$ species. The narrow signals ($\Delta\gamma_{1/2} < 10$ Hz) of both kinds of cyano ligands coordinated to Pt in the complex (centered at 97 ppm (^{13}C : $^2J_{\text{Tl}-\text{C}} = 255$ Hz, $^1J_{\text{Pt}-\text{C}} = 843$ Hz) and 116 ppm (^{13}C : $^1J_{\text{Tl}-\text{C}} = 7270$ Hz, $^1J_{\text{Pt}-\text{C}} = 742$ Hz, hardly visible) for the four equatorial and one axial cyanides, respectively) and the $\text{Pt}(\text{CN})_4^{2-}$ species (centered at 130 ppm, $^1J_{\text{Pt}-\text{C}} = 1031$ Hz) indicate the relative inertness of the Pt–C bonds. In contrast, the labile CN^- ligands coordinated to the thallium site of the bimetallic complex and $\text{Tl}(\text{CN})_4^-$, together with the free cyanides, have only one, almost invisible, time-averaged broad signal ($\Delta\gamma_{1/2} > 300$ Hz) at around 135 ppm.

The above features imply that the labile thallium center can readily accommodate the necessary changes in both the composition and geometry during the formation of the bimetallic complex, while the dynamic properties of the platinum center must supersede the overall reaction. In other words, the crucial point of the mechanism is how the somewhat inert $\text{Pt}(\text{CN})_4^{2-}$ complex is activated during the formation of the bimetallic complex. In general, we can consider two possibilities for the sequence of elementary reactions constituting the reaction mechanism: the formation of a transient pentacoordinated cyano complex of platinum(II) precedes the metal–metal bonding (reactions 7–9) or the Pt–Tl bond is formed first, which activates an axial site (trans to the thallium atom) of the “partially” oxidized platinum (vide infra).

Experiments have been carried out to confirm the existence of the $[\text{Pt}(\text{CN})_5]^{3-}$ cyano complex of Pt(II) with a large excess of cyanide ion ($[\text{Pt}(\text{CN})_4^{2-}]/[\text{CN}^-]_{\text{tot}} = 1:26$) using the ^{195}Pt NMR method. No other signal was detectable than the one of $\text{Pt}(\text{CN})_4^{2-}$ ($\delta = -215 \pm 1$ ppm). No substantial change was observed either in the chemical shift or in the intensity of this signal. Kinetic studies on the cyanide exchange reaction between the $\text{Pt}(\text{CN})_4^{2-}$ complex and the bulk cyanide ions confirmed an associative mechanism, implying the formation of a pentacyano intermediate,^{32a} even though the intermediate could not be experimentally detected.^{32b} Probably this intermediate is not identical with a thermodynamically stable $\text{Pt}^{\text{II}}(\text{CN})_5^{3-}$ species. The ligand exchange reaction is reasonably fast, $k_{\text{ex}} = 26 \text{ M}^{-1} \text{ s}^{-1}$,^{32a} and the formation of the Pt–Tl complex may proceed via the same transient species (see reaction 7). In alkaline solution, the next step would be the metal–metal bond formation and incorporation of the axial cyanide into the inner sphere of the Pt center by reaction between $\text{Pt}(\text{CN})_5^{3-}$ and $\text{Tl}(\text{CN})_4^-$ (reaction 8), which is followed by the fast release of a cyanide ion from the thallium side of intermediate a (reaction 9).

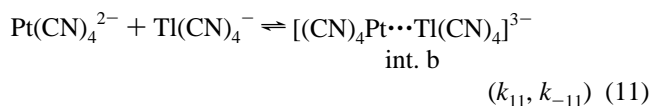


Due to the noted lability of the thallium(III) center, reaction 9 is expected to be a fast equilibrium step. Therefore, we propose that reaction 8 is the rate-determining step in this mechanism. Provided that the transient pentacyano Pt species and the intermediate are in steady state, the following expression can be derived for k_1^{a} and k_{-1}^{a} (see SI):

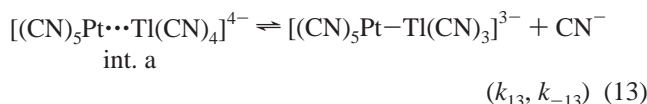
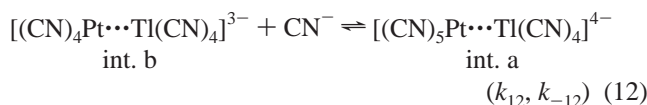
$$k_1^{\text{a}} = \frac{k_7 k_8 k_9}{k_{-7} k_{-8} + k_{-7} k_9 + k_8 k_9 [\text{Tl}(\text{CN})_4^-]} \quad (10)$$

$$k_{-1}^{\text{a}} = \frac{k_{-7} k_{-8} k_{-9}}{k_{-7} k_{-8} + k_{-7} k_9 + k_8 k_9 [\text{Tl}(\text{CN})_4^-]}$$

The alternative mechanism assumes that the sequence of the metal–metal bond formation and the coordination of the fifth cyanide ion to Pt(II) is reversed:



(32) (a) Pesek, J. J.; Mason, W. R. *Inorg. Chem.* **1983**, *22*, 2958–2959. (b) Monlien, F. J.; Helm, L.; Abou-Hamdan, A.; Merbach, A. E. *Inorg. Chem.* **2002**, *41*, 1717–1727.



In this sequence, both the formation of the metal–metal bond and the release of the cyanide ion from the thallium site (reactions 11 and 13, respectively, note that 13 is identical to 9) are assumed to be fast processes, while coordination of the fifth cyanide to the platinum atom (reaction 12) is the rate-determining step. The corresponding expressions for k_1^a and k_{-1}^a are given as follows:

$$k_1^a = \frac{k_{11}k_{12}k_{13}}{k_{-11}k_{-12} + k_{-11}k_{13} + k_{12}k_{13}[\text{CN}^-]} \quad (14)$$

$$k_{-1}^a = \frac{k_{-11}k_{12}k_{13}}{k_{-11}k_{-12} + k_{-11}k_{13} + k_{12}k_{13}[\text{CN}^-]}$$

In the case of the square-planar $\text{Pt}(\text{CN})_4^{2-}$ complex, the HOMO, which is essentially the platinum $5d_{z^2}$ orbital,^{7,33} seems to be well suited for the formation of the metal–metal bond and can overlap with the empty $6s$ orbital of thallium(III). Since this is not a ligand substitution, rather an electron transfer step, it does not require ligand field activation and may proceed relatively quickly.

The formation of the metal–metal bond can be considered as a partial electron transfer from Pt(II) to Tl(III) which, in turn, strongly perturbs the d^8 electron configuration of platinum. As a result, the coordination geometry changes and the electron density decreases on the Pt center. Consequently, the trans position to the metal–metal bond becomes suitable for a nucleophilic attack by the ligand. The coordination of an additional nucleophilic ligand to the Pt center can stabilize the metal–metal bond by making more favorable the electron transfer between Pt(II) and Tl(III) resulting in the C–Pt–Tl entity with a three-center four-electron bonding.¹⁵ The increased electron density on the Tl center also promotes the fast release of a cyanide from the thallium coordination sphere in intermediate a (reaction 9 or 13).

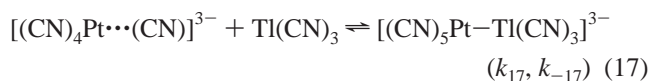
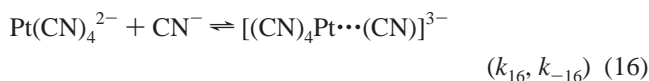
The rate of the acidic reaction path is independent from the concentration of cyanide ion (cf. eq 5). Formally the rate law is consistent with a direct reaction between $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Tl}(\text{CN})_4^-$ followed by an intramolecular cyanide transfer between the metal centers. In this case, the corresponding metal–metal bonded intermediate would comprise pentacoordinated platinum and thallium centers. Most likely the repulsion between the cyanide ligands coordinated to the metal ions would efficiently hinder such an interaction. Another obstacle for the reaction can simply arise from electrostatic repulsions between these two cyanide complexes

with the respective charges of -2 and -1 . This should substantially decrease the probability of the interaction between the reacting species. Finally, this path would require the rearrangement of the cyanide ligands around the Pt center, which does not seem to be possible on the basis of earlier results. Therefore, we reject the possibility of a direct reaction between the two reactants and propose that the linear dependence on the concentration of $\text{Tl}(\text{CN})_4^-$ corresponds to a mechanism which includes the reaction of the $\text{Tl}(\text{CN})_3$ complex. This species is always in fast equilibrium with $\text{Tl}(\text{CN})_4^-$ (reaction 15),¹⁷ which is controlled by the concentration of free cyanide ion (i.e., pH, vide supra).

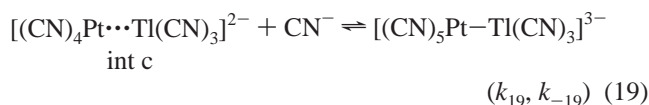
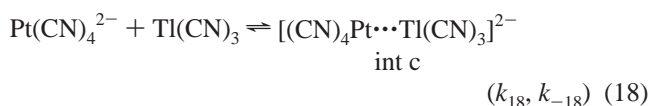


$$K_{\text{Tl}(\text{CN})_4^-} = \frac{[\text{Tl}(\text{CN})_4^-]}{[\text{Tl}(\text{CN})_3][\text{CN}^-]}$$

In analogy with the alkaline path, the first step of the overall process can be the formation of either the pentacyano or a metal–metal bonded intermediate. The alternative kinetic models are as follows:



or



By assuming steady state for the intermediates, the following expressions are obtained for k_1^b and k_{-1}^b

$$k_1^b = \frac{k_{16}k_{17}}{k_{-16} + k_{17}[\text{Tl}(\text{CN})_3]} \frac{1}{K_{\text{Tl}(\text{CN})_4^-}} \quad (20)$$

$$k_{-1}^b = \frac{k_{-16}k_{-17}}{k_{-16} + k_{17}[\text{Tl}(\text{CN})_3]}$$

or

$$k_1^b = \frac{k_{18}k_{19}}{k_{-18} + k_{19}[\text{CN}^-]} \frac{1}{K_{\text{Tl}(\text{CN})_4^-}} \quad (21)$$

$$k_{-1}^b = \frac{k_{-18}k_{-19}}{k_{-18} + k_{19}[\text{CN}^-]}$$

k_{obs} should reach a limiting value by increasing the concentration of $[\text{CN}^-]$ (eqs 14 and 21), $[\text{Tl}(\text{CN})_4^-]$ (eq 10), and

(33) Ziegler, T.; Nagle, J. K.; Snijders, J. G.; Baerends, E. J. *J. Am. Chem. Soc.* **1989**, *111*, 5631.

$[Ti(CN)_3]$ (eq 21). In principle, this offers a possibility to test the validity of the alternative kinetic models by simply measuring k_{obs} as a function of $[Ti(CN)_4^-]$, $[Ti(CN)_3]$, or $[CN^-]$ while keeping the concentrations of the other reactants constant. Because of experimental limitations, our attempts to use sufficiently high concentrations of these species to demonstrate the retarding effects failed. Consequently, experimental evidence is not available to prove or exclude explicitly any of the alternative reaction paths. The previous considerations imply that HCN is unreactive despite that it is the dominant form of the free ligand under slightly acidic conditions. The HCN path would introduce a pH dependence of the reaction rate. The fact that the small variation of k_{obs} as a function of pH can sufficiently be explained by the contribution of the alkaline rate (eq 6) supports the above assumption. It follows that CN^- is several orders of magnitude more reactive than HCN. Such a difference in the reactivity of different forms of the same ligand is not unusual in ligand substitution reactions.

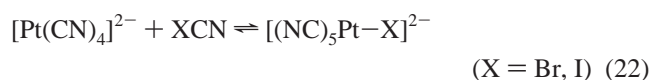
To separate the individual rate constants in eqs 10, 14, 20, and 21, the rate constants or the equilibrium constant for at least one of the reaction steps should be known independently. Unfortunately, only rough estimates can be given for some of these parameters. Thus, it seems to be a reasonable assumption that the value of k_7 is similar to that of the cyanide exchange rate constant of the $Pt(CN)_4^{2-}$ complex and the lower limits for the stability constants of the pentacyano complex and the metal–metal bonded intermediates can be estimated by using the Fuoss equation.³⁴ Nevertheless, the uncertainties associated with these parameters do not allow any further elaboration of the individual rate constants.

Despite the obvious limitations, the previous considerations provide good interpretation of the kinetic data in the acidic-alkaline pH region and, in a broader sense, are consistent with previous results on the kinetic and structural features of platinum(II) and thallium(III) complexes in related systems.

As an alternative to the mechanisms via the direct formation of the nonbuttressed Pt–Tl bond, it can also be stipulated that a cyano-bridged intermediate forms prior to the metal–metal bond. Bridging is an important mode of coordination of the cyanide ligand, which is particularly often recognized in oligometallic systems of platinum(II) complexes.^{35–38} Electron transfer between the coupled metal ions could then be mediated via a bridging cyanide ion.^{35,39,40} In this case, the reaction between $Pt(CN)_4^{2-}$ and $Tl(CN)_4^-$ complexes would yield a cyano-bridged transient, $\{(CN)_4Pt \cdots NC-Tl(CN)_3\}^{3-}$. However, a plausible reaction

path does not seem to be available to facilitate the intramolecular rearrangement of this hypothetical species into the final metal–metal bonded complex and transformation of this intermediate via a dissociative path would ultimately lead to one of the mechanisms proposed above. Consequently, the formation of the cyano-bridged complex was rejected from our model. The fact that the rate law is first order in $[CN^-]$ is direct evidence to support this assumption.

The results presented here can conveniently be compared to previous literature data. Considering the “platinum part” of the bimetallic complexes, reaction 1 resembles oxidative addition reactions of $Pt(CN)_4^{2-}$. Although a uniform mechanism does not hold for all oxidative addition reactions, certain similarities can be recognized.^{41,42} Among others, the reactions leading to the formation of pentacyano complexes are the best for comparison:^{43–46}



As in the case of thallium(III) cyano complexes, the rate of the reaction between halogen cyanides and tetracyanoplatinate is dependent on $[CN^-]$ and/or pH and the experimental rate law is

$$-\frac{d[Pt(CN)_4]^{2-}}{dt} = k[Pt(CN)_4^{2-}][CN^-][XCN] \quad (23)$$

where $k = 8.2 \times 10^{-5} \text{ M}^{-2} \text{ s}^{-1}$ and the activation entropy, $\Delta S^\ddagger = -5.6 \text{ cal/mol}$,⁴⁷ indicates an associative mechanism for the reaction when $X = I$.⁴⁴ Negative activation entropy has been published for oxidative addition reactions of several other square-planar complexes.^{41b} In this respect, similar to the halogen cyanides, the $Tl(CN)_4^-$ complex can be considered as an oxidative addition agent. The difference between oxidative reactions of halogen cyanides and thallium(III) tetracyano complex with $Pt(CN)_4^{2-}$ is that in the former case platinum is completely oxidized from Pt^{II} to Pt^{IV} , while in the latter case the oxidation state of platinum is probably best described as intermediate between II and IV.^{9,10}

It is worth mentioning that the iodide catalysis of the reaction of $Ir(cod)(o\text{-phen})^+$ with CH_3I ⁴⁸ resembles the $[CN^-]$ dependence in the studied reaction between $Pt(CN)_4^{2-}$ and $Tl(CN)_4^-$. The mechanism suggested for that reaction also postulates an intermediate with extended coordination num-

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(45) Osso, R.; Rund, J. V.; *J. Coord. Chem.* **1978**, *8*, 169.

(46) Busev, A. I.; Babkov, A. V.; Busurmanova, B. T. *Kinet. Catal.* **1975**, *16*, 45–49.

(47) The meaning of ΔS^\ddagger is not clear because it is related to k , which is not a single rate constant but a combination of various temperature-dependent parameters: $k = k_4K_2K_3$.

(48) De Woal, D. J. A.; Gerber, T. I. A.; Louw, W. J. *Inorg. Chem.* **1982**, *21*, 1260.

ber of Ir(I). The first step in that system is the coordination of I^- and not the electron-transfer process. Similar mechanisms have also been reported for the formation of platinum–tin metal–metal bonded complexes.^{49,50}

One more example for the metal–metal bonding of trivalent thallium is its interaction with another d^8 cation, iridium(I). Addition of thallium(III) acetate to the square-planar $Ir(CO)Cl(PPh_3)_2$ complex results in the formation of $[(CH_3CO_2)_2Tl-\mu(O_2CCH_3)Ir(CO)(PPh_3)_2](O_2CCH_3)$ with a short (2.611 Å) Ir–Tl bond supported by an acetate bridge.⁵¹ The coordination number of the iridium atom increases to six which, together with other pieces of spectroscopic evidence, clearly indicates the oxidation of the iridium center in the binuclear complex. Similar to the Pt–Tl assemblies described above, the Ir–Tl compound was viewed as a result of oxidative addition of thallium(III) acetate to the square-planar iridium(I) complex leading to the Ir–Tl bond.

Concluding Remarks

As a continuation of our structural and equilibrium studies on the unusual platinum–thallium bonded cyano compounds, we evaluated the formation kinetics of the $[(CN)_5PtTl(CN)_3]^{3-}$ complex. Two possible pathways have been suggested for the reaction, which seems to be an oxidative addition process. Two important steps need to occur during the formation of the complex: (i) metal–metal bond formation and (ii) the

coordination of the fifth cyanide to the platinum center. Regardless of the actual pH, the main difference between the two mechanisms is the sequence of i and ii; however, the order of the elementary reactions cannot be resolved.

Aqueous solution of the $[(CN)_5Pt-Tl(CN)_3]^{3-}$ complex is stable at room temperature for months, but it decomposes when heated. The products of decomposition are $Pt^{IV}(CN)_6^{2-}$ and Tl^I . This observation indicates that the bimetallic complex is in fact a metastable intermediate in the course of a two-electron oxidation of Pt^{II} by Tl^{III} .¹⁸ The specific feature of this system is that the complementary two-electron transfer reaction between the Pt^{II}/Pt^{IV} and Tl^{III}/Tl^I complex stops at “halfway” and long-lived Pt–Tl bonded intermediate species are formed. To explore the intimate nature of this process, further studies are needed to describe the electron structure of the metal–metal bond. The structure of the linear $NC-Pt-Tl$ entity is the subject of particular interest because of possible stabilizing effects on the metal–metal bond.

Acknowledgment. The authors are grateful to the Hungarian Science Research Foundation (OTKA, Project T 038296 and M 028244) and the Swedish Natural Research Council for financial support. P.N. thanks ERASMUS for traveling support.

Supporting Information Available: Table of concentrations, observed and calculated k_{obs} values and their deviations, derivation of the rate expressions on the basis of the models, and k_{obs} vs $[Tl(CN)_4^-]$ plots both at acidic and at alkaline pH. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC034676H

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