A New Class of Oligonuclear Platinum-Thallium Compounds with a Direct Metal–Metal Bond

3. Unusual Equilibria in Aqueous Solution[◇]

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A new series of four binuclear platinum-thallium cyano compounds containing a direct and unsupported by ligands metal–metal bond has been prepared in aqueous solution. These compounds are represented by the formula $[(NC)_5Pt{-}Tl(CN)_{n-1}]^{(n-1)-}$ (n = 1–4 for compounds **I**, **II**, **III** **IV,** respectively) and $[(NC)_5Pt{-}Tl{-}Pt(CN)_5]^{3-}$ (for compound **V**). The oligonuclear complexes are synthesised according to the reaction $m\mathrm{Pt(CN)_4}^{2-} + \mathrm{Tl}^{3+} + n\mathrm{CN}^- \rightleftharpoons [\mathrm{Pt}_m\mathrm{Tl(CN)}_{4m+n}]^{3-2m-n}$. Thus, there occurs a change of the coordination number of the Pt center from four (square planar) to six (octahedral). Consequently, the formation of binuclear platinum-thallium cyano compounds involves at least two steps: (i) formation of metal–metal bond and (ii) formation of $(NC)_5Pt-$ unit by a cyanide transfer process. – The complexes exist in an equilibrium, which also includes the parent complexes $\mathrm{Pt(CN)_4}^{2-}$ and $\mathrm{Tl(CN)}_n{}^{3-n}$ (n = 0–4), and can be controlled by varying the cyanide concentration and/or pH of the solution. The stability constants of the compounds $\beta_N = [\mathrm{Pt}_m\mathrm{Tl(CN)}_{4m+n}{}^{3-2m-n}]\ /\ \{[\mathrm{Pt(CN)_4}^{2-}]^m\cdot[\mathrm{Tl}^{3+}]\cdot[\mathrm{CN}^-]^n\}$ have been determined by means of multinuclear NMR (^{195}Pt, ^{205}Tl): $\log\beta_N$ = 19.9±0.4, 30.7±0.3, 38.6±0.3, and 44.8±0.2 for **I**, **II**, **III**, and **IV** (m = 1, n = 1–4), and 32.1±0.3 for **V** (m = 2, n = 2), respectively, (in 1 M $NaClO_4$ as ionic medium, at 25 °C). To our knowledge, the present work constitutes the first detailed equilibrium study of metal–metal bonded compounds; it indicates that also other cluster formation reactions described in the literature may represent real equilibria.

Introduction

Starting from the report of Nagle et al. on the six-coordinated platinum in the structure of *trans*-$Tl_2Pt(CN)_4$,[3] a few oligometallic compounds containing platinum and thallium have been synthesised and their properties studied.[4][5][6][7][8][9] Recently, we have published a study of new binuclear platinum-thallium cyano compounds containing a direct metal–metal bond.[1] Their structure has been studied in solution[2] as well as in the solid state.[10] In the present study a new aspect of these small clusters' chemistry is explored, namely their equilibrium behaviour in aqueous solution. The data on reversible equilibrium processes for metal–metal bonded compounds is practically non-existent.[11][12][13] Also for metal–carbon bonded compounds (excluding cyano complexes) the information is very scarce.[14][15] Equilibrium models, which are routinely used in coordination chemistry, would provide obvious advantages also for cluster chemistry, e.g. to increase the yield of a reaction by shifting the equilibrium in the direction of required species using the law of mass action in a quantitative way, or for catalytic studies providing speciation of the potentially active complexes, thus allowing the chemist to tune their redox potential, selectivity, etc.

Our interest on two-electron transfer reactions in solution prompted us to study the equilibria of the $\mathrm{Tl^{III}}$–$\mathrm{Pt^{II}}$–$\mathrm{CN^-}$ system in water. The advantage of these components for a multinuclear NMR study is obvious, all atoms have suitable NMR active nuclei (see in refs.[1] and[2]). ^{205}Tl NMR is superior in sensitivity, and its huge chemical shift scale provides slow exchange regimes for the different species, thus allowing to follow the concentration distribution of the formed clusters. A further advantage of the direct spectroscopic detection of the different species was that the evaluation of the overall stability constant values of this relatively complicated system was possible without any sophisticated data treatment, using only molar ratios calculated from the NMR integrals and the mass balance equations. In this context, the structural change in the geometry of the platinum coordination sphere from four- to six-coordination in a two-step formation reaction of the platinum–thallium cluster is also discussed.

Results and Discussion

Preliminary experiments aimed at finding new complexes[2] indicated that the speciation of the Pt-Tl bimetallic complexes varies at different total concentrations of the

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components, Tl^{3+}, $Pt(CN)_4^{2-}$, CN^-, and H^+. Changing the concentration of any of the components shifted the distribution of the reactants and/or products, and demonstrated the existence of several types of chemical equilibria in the solutions.

In solutions with molar ratio Pt/Tl ≤ 1, bimetallic compounds are present only as binuclear species **I**−**IV**, at Pt/Tl > 1 a trimer **V** can be formed. The formation of the complexes in solution can be described by the following equilibrium:

$$m\,Pt(CN)_4^{2-} + Tl^{3+} + n\,CN^- \rightleftharpoons [Pt_mTl(CN)_{4+n}]^{(n-1)-} \quad (1)$$

giving the following overall stability constant:

$$\beta_N = [Pt_mTl(CN)_{4m+n}{}^{3-2m-n}] / \{[Pt(CN)_4^{2-}]^m \cdot [Tl^{3+}] \cdot [CN^-]^n\} \quad (1a)$$

where $m = 1$, $n = 1, 2, 3$, and 4 for **I**, **II**, **III**, and **IV**; and $m = 2$, $n = 2$ for **V**, respectively. The following simultaneous equilibria taking place in this system must also be considered:

$$Tl^{3+} + n\,CN^- \rightleftharpoons Tl(CN)_n^{3-n} \quad (2)$$

with $\beta_n = [Tl(CN)_n^{3-n}] / \{[Tl^{3+}]\cdot[CN^-]^n\}$,[20] and

$$CN^- + H^+ \rightleftharpoons HCN \quad (3)$$

with $K_H = K_a^{-1} = [HCN] / \{[CN^-][H^+]\}$.[21]

Although the stepwise formation/dissociation of platinum(II) cyano complexes could also be considered, the only species detected in ^{195}Pt-NMR spectra at the current experimental conditions were $Pt(CN)_4^{2-}$ and $[Pt_mTl(CN)_{4m+n}]^{3-2m-n}$ (and in some solutions also $Pt(CN)_6^{2-}$, which formed as a product of a slow photo-induced irreversible redox reaction). This finding is in accordance with the known properties of the complex, $Pt(CN)_4^{2-}$, namely its high stability (different values of $\log\beta_4$ can be found in the literature, ranging from 35 up to 65)[22] and kinetic inertness.[23] Based on these facts the species $Pt(CN)_4^{2-}$ was treated as a stable component.

The "addition reactions" between the complexes $Pt(CN)_4^{2-}$ and $Tl(CN)_n^{3-n}$ resulting in binuclear complexes:

$$Pt(CN)_4^{2-} + Tl(CN)_n^{3-n} \rightleftharpoons [PtTl(CN)_{4+n}]^{(n-1)-} \quad (4)$$

can be represented by the equilibrium constants,

$$K_N^{\mathrm{add}} = [PtTl(CN)_{4+n}{}^{(n-1)-}] / \{[Pt(CN)_4^{2-}]\cdot[Tl(CN)_n^{3-n}]\} \quad (4a)$$

for $n = 1, 2, 3$, and 4, referring to complexes **I**, **II**, **III**, and **IV**, respectively. These constants can be calculated from the signal integrals of the Tl-containing species and the concentration of $Pt(CN)_4^{2-}$. The latter can be calculated from the following mass balance equation:

$$[Pt]_{tot} = [Pt(CN)_4^{2-}] + [\mathbf{I}] + [\mathbf{II}] + [\mathbf{III}] + [\mathbf{IV}] + [Pt(CN)_6^{2-}] \quad (5)$$

where the concentration of $Pt(CN)_6^{2-}$ can be assumed to be practically equal to that of Tl^+, due to the redox reaction: $Tl^{III} + Pt^{II} \rightleftharpoons Tl^+ + Pt^{IV}$. Equilibrium constants were determined and are: $\log K_{II}{}^{\mathrm{add}} = 4.2$ (±0.3), (based on 10 experimental points); $\log K_{III}{}^{\mathrm{add}} = 3.6$ (±0.3), (3 points); $\log K_{IV}{}^{\mathrm{add}} = 2.3$ (±0.1), (21 points). The small number of points for measuring $\log K_{III}{}^{\mathrm{add}}$ is due to the experimental finding that the complex $Tl(CN)_3$ is a minor species existing in an unbuffered region of the titration curve. $Tl(CN)^{2+}$ was not observed at any of the current experimental conditions; hence, a direct determination of $K_I{}^{\mathrm{add}}$ was not possible. The values of stability constants obtained for the complexes **II**−**IV** demonstrate high thermodynamic stability of the bimetallic Pt-Tl complexes as compared to the reagents.

The formation of the bimetallic species, **II**, **III**, and **IV** can also be described by a stepwise coordination of CN^- ions to **I**:

$$[PtTl(CN)_{4+(n-1)}]^{(n-2)-} + CN^- \rightleftharpoons [PtTl(CN)_{4+n}]^{(n-1)-} \quad (6)$$

giving equilibrium constants, $K_N = [PtTl(CN)_{4+n}{}^{(n-1)-}] / \{[PtTl(CN)_{4+(n-1)}{}^{(n-2)-}]\cdot[CN^-]\}$ for $n = 2, 3$ and 4, referring to the complexes $n =$ **II**, **III**, and **IV**, respectively. These constants, K_N, can be calculated from the signal integrals of the Pt-Tl-containing species, measured for suitable titration points and using $[CN^-]$ calculated from the mass balance equation:

$$[CN]_{tot} = [CN^-] + [HCN] + n\,[Tl(CN)_n^{3-n}] + 4\,[Pt(CN)_4^{2-}] + 5\,[\mathbf{I}] + 6\,[\mathbf{II}] + 7\,[\mathbf{III}] + 8\,[\mathbf{IV}] + 6\,[Pt(CN)_6^{2-}] \quad (7)$$

It should be noted, that the protonation equilibrium must also be considered when calculating values of K_N. Free cyanide concentrations were calculated by means of Eq. 3 from the equilibrium hydrogen ion concentration, $[H^+]$, obtained from the pH-potentiometric titrations (see Supplementary Material). The calculated values are: $\log K_{II} = 10.8$ (±0.2), (24 experimental points) and $\log K_{III} = 6.6$ (±0.4), (5 points). The latter one calculated for 5 points is less reliable; for $\log K_{IV}$ no trustworthy value could be calculated, due to the same reasons as discussed above for $\log K_{III}{}^{\mathrm{add}}$. The trend of the constants follows the normal decrease of the stepwise stability constants, although the decrease is somewhat smaller compared to the corresponding values for the parent complexes, $Tl(CN)_2^+$ ($\log K_2 = 13.2$), $Tl(CN)_3$ ($\log K_3 = 8.5$).[20] The pronounced weakening of the bond between thallium and cyanide ligands in **II** and **III** compared to $Tl(CN)_2^+$ and $Tl(CN)_3$, respectively, can be attributed to the strong influence of the $(NC)_5Pt-$ unit coordinated to the thallium atom in these complexes.

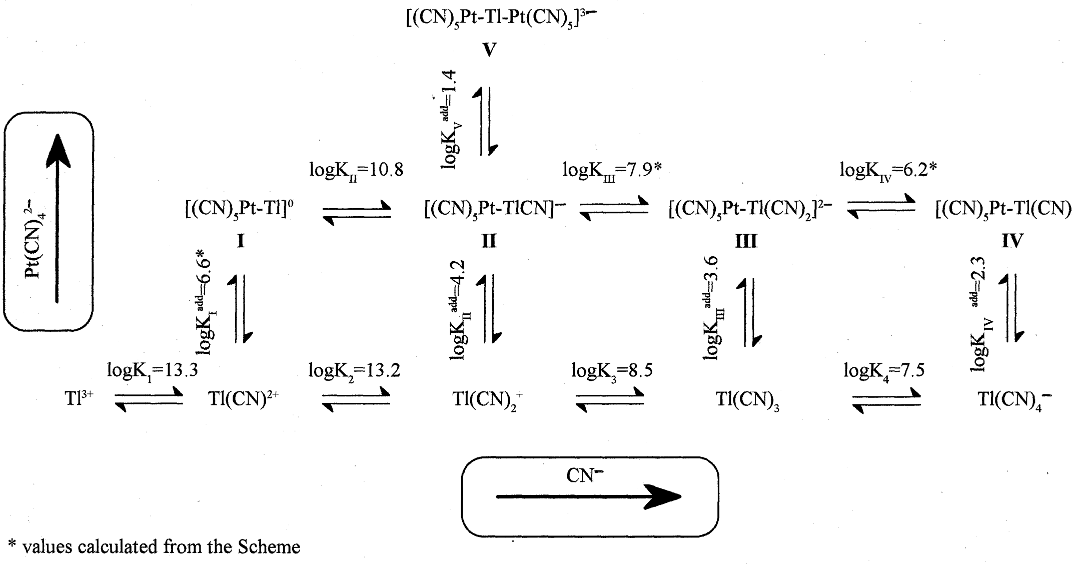
In addition, a trinuclear complex **V** with the formula $[(NC)_5Pt-Tl-Pt(CN)_5]^{3-}$ is formed in solutions where the Pt/Tl ratio is larger than 1. This complex can be considered as an adduct of **II** and $Pt(CN)_4^{2-}$:

$$[PtTl(CN)_6]^- + Pt(CN)_4^{2-} \rightleftharpoons [Pt_2Tl(CN)_{10}]^{3-} \quad (8)$$

with an equilibrium constant,

$$K_V{}^{\mathrm{add}} = [Pt_2Tl(CN)_{10}{}^{3-}] / \{[Pt(CN)_4^{2-}]\cdot[PtTl(CN)_6^-]\} \quad (8a)$$

$K_V{}^{add}$ can easily be calculated from the integral ratios of **II** and **V** (R = [**II**]/[**V**]) measured by ^{205}Tl NMR, and from the equilibrium concentration of $Pt(CN)_4^{2-}$ derived from ^{195}Pt NMR; $K_V{}^{add} = 1/(R\cdot[Pt(CN)_4^{2-}])$. It can be noted that no additional data are needed, and the experimental conditions for samples D1−D5 were selected in order to achieve comparable values of integrals for **II** and **V**, and to obtain measurable integrals for $[Pt(CN)_4^{2-}]$ in order to minimize the uncertanties related to the integration (see Supplementary Material). Samples, D2−D5 are in fact a serial dilution of D1. The higher the total concentrations the larger the fraction of the trimer. From these data (5 experimental points), $K_V{}^{add} = 1.44 \pm 0.03$ was calculated (see Scheme).



* values calculated from the Scheme

The equilibria describing the chemical system (components: $Pt(CN)_4^{2-}$, Tl^{3+} , CN^-, and H^+) are shown in the Scheme. It shows how the reactions 4, 6, and 8 result in formation of the different Pt-Tl complexes. These equilibria are related to each other and some of them can be calculated independently. From the known stepwise stability constants ($\log K_n$) for the parent complexes, $Tl(CN)_n{}^{3-n}$,[20] and the values of $\log K_{II}{}^{add}$, $\log K_{III}{}^{add}$, $\log K_{IV}{}^{add}$, and $K_V{}^{add}$ determined in this work, we obtain

$$\log K_{III} = \log K_3 + \log K_{III}{}^{add} - \log K_{II}{}^{add} = 7.9 \text{ and}$$
$$\log K_{IV} = \log K_4 + \log K_{IV}{}^{add} - \log K_{III}{}^{add} = 6.2.$$

In the following, when calculating the overall stability constants β_N, this value of $\log K_{III}$ is used instead of the directly determined and less reliable one (vide supra).

In addition the Scheme gives one more constant which is not directly measurable:

$$\log K_I{}^{add} = \log K_2 + \log K_{II}{}^{add} - \log K_{II} = 6.6.$$

These data can easily be converted to overall stability constants, $\log\beta_N = \log K_N{}^{add} + \log\beta_n$ (N = **I−IV**) and $\log\beta_V = \log\beta_{II} + \log K_V{}^{add}$ (cf. Eq. 1a); the values of logβ are given in Table 1.

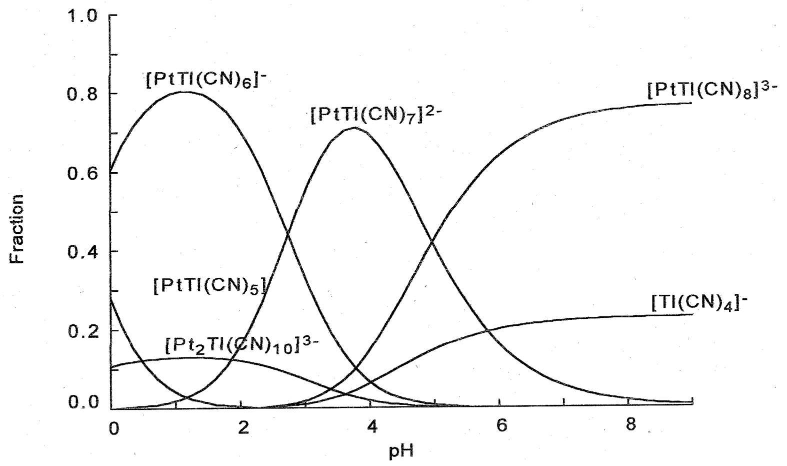
A typical distribution diagram of the studied chemical system, calculated using the data of Table 1 and ref.[20], is given in Figure 1. The increase of the free cyanide ion concentration with increasing pH causes further coordination of CN^- to the thallium atom of the binuclear Pt-Tl species and thus the equilibrium shifts towards the formation of Pt-Tl complexes with a higher number of cyanide ligands. In the presence of excess $Pt(CN)_4^{2-}$, compound **II** can also be transferred to **V**, but the formation of the trinuclear complex might be supressed by CN^- competition resulting in formation of compound **III**. At higher pH, the mononuclear complexes of platinum $[Pt(CN)_4^{2-}]$ and thallium $[Tl(CN)_4^-]$ are also present (i.e. equilibrium 4 is shifted to the left). Decrease of the pH shifts reaction 4 to the right, showing that the metal−metal bond formation in aqueous solution is reversible. Certainly, varying the pH shifts also

Table 1. Overall stability constants[a][b] of the Pt-Tl complexes I−V. $\beta_N = [Pt_mTl(CN)_{4m+n}{}^{3-2m-n}] / \{[Pt(CN)_4^{2-}]^{m-}\cdot[Tl^{3+}]\cdot[CN^-]^n\}$, where m = 1, n = 1, 2, 3, and 4 for **I**, **II**, **III**, and **IV**; and m = 2, n = 2 for **V**, respectively. Temperature 25 °C, ionic medium ca. 1 M $NaClO_4$

Complex	$\log\beta_N$
I	19.9±0.4
II	30.7±0.3
III	38.6±0.3
IV	44.8±0.2
V	32.1±0.3

[a] Uncertainties are averaged deviations from the mean value calculated for the individual titration points; and attributed to uncertainties in the $\log K_N{}^{add}$ values (cf. Eqs. 4a and 8a), except for the error in **I**, which was estimated as the sum of uncertainties in $\log K_{II}{}^{add}$ and $\log K_{II}$. − [b] The value of $\log K_H = 9.3$ (cf. eq 3) was estimated from pH-potentiometric titration (titration C) and was used for the calculation of the constants, K_N. Note that the ionic strength, $I \approx 1$ M, was varying slightly during the titration and could reach up to 1.3 at high pH values.

Figure 1. Typical distribution of thallium-containing species in aqueous solution as a function of pH, as calculated from the determined stability constants (Table 1)[a]



[a] $[Pt]_{tot}$ = 40 mM, $[Tl]_{tot}$ = 30 mM, $[CN]_{tot}$ = 280 mM.

the equilibrium of reaction 6, similarly as for the parent $Tl(CN)_n^{3-n}$ species.

These thermodynamic data (K_N^{add}) could be used as a quantitative measure of the stability or strength of the Pt−Tl bond only if the simple formation of an adduct between platinum and thallium cyanides took place by means of the reaction:

$$Pt(CN)_4^{2-} + Tl(CN)_n^{3-n} \rightleftharpoons (NC)_4Pt{-}Tl(CN)_n^{(n-1)-} \quad (9)$$

and if the entropy term is negligible. However, the structural data discussed in our recent paper[2] show that in all the bimetallic complexes five cyanides are coordinated directly to the Pt-center, and this $(NC)_5Pt-$ unit is, in turn, coordinated to the Tl atom. The species $[Pt^{II}CN)_5]^{3-}$ has not been reported previously and it is likely that it does not exist; accordingly, no formation constant has been measured.[24] When the free $[CN^-]$ is decreased, the equilibrium is shifted towards species with lower cyanide content, down to complex **I** with no cyanide ligands coordinated to the thallium atom, whereas the $(NC)_5Pt-$ unit remains unchanged. Thus, the stability constant for the coordination of the "fifth" cyanide to the Pt atom must be larger compared to all cyanides bound to thallium in the binuclear compounds.

It seems unreasonable that an extra cyanide ligand would be coordinated to the $Pt^{II}(CN)_4^{2-}$ complex without oxidation of platinum; hence, the formation of the $(NC)_5Pt-$ unit must be preceded or accompanied by an electron transfer from Pt to Tl leading to the formation of a Pt−Tl bond. Therefore, reaction 4 should involve at least two steps: (i) formation of metal−metal bond according to reaction 9 and (ii) formation of $(NC)_5Pt-$ unit by a cyanide transfer reaction. Whether these reactions are simultaneous or not should be subject of further study.

It can be noted that most information on complexes with metal−metal bonds in the literature has been obtained for the solid state; the reported solution studies were aimed mainly at structural characterisation of the species. In this context, the qualitatively studied $[Rh(CO)_2Cl]_2$−$[Co(CO)_4]^-$ system in toluene can be mentioned;[11] it exhibits some features similar to the bimetallic Pt-Tl cyanide compounds. Heteropolynuclear complexes formed in the Rh-Co solutions are in equilibrium which is governed by the Rh/Co ratio. The presumed bimetallic compound $(R_4N)[Rh(CO)_2ClCo(CO)_4]$ decomposes by addition of either Cl^- or OH^- ions to give mononuclear species. In another carbonyl mixed metal cluster, $[Re_7C(CO)_{21}Tl]^{2-}$, dissociation of μ_3-Tl^I was followed by infrared spectroscopy in acetone and a dissociation constant $K = 2.1 \cdot 10^{-3}$ M was calculated.[13] Also for the related cyano metal clusters equilibrium data are very scarce. A study of a stepwise coordination of cyanide to Mo−Mo and W−W bonded clusters has been published, but a formation of the metal−metal bond is not involved in the qualitative description of the equilibria.[12][25] In another study, an estimated stability constant (10^6) has been reported for the CN-bridged iron-platinum species.[26]

In the case of metal−carbon bonds there are a few papers containing equilibrium data. In our earlier work[14][15] we characterized the formation of monoketonato-thallium(III) ion in aqueous solution. In this equilibrium ketonato and the chloride ligands are in competition for Tl^{III}.

Conclusions

Reaction between $Pt(CN)_4^{2-}$ and $Tl(CN)_n^{3-n}$ ($n = 1-4$) complexes in aqueous solution results in the formation of a family of heteropolynuclear cyano complexes. Depending on the molar ratio Pt/Tl, cyanide concentration and pH, four binuclear complexes **I**−**IV** with the general composition $[(CN)_5Pt{-}Tl(CN)_{n-1}]^{(n-1)-}$ ($n = 1-4$) and a trinuclear species **V** with the formula $[(NC)_5Pt{-}Tl{-}Pt(CN)_5]^{3-}$ can be obtained.

If kept in dark, the complexes are in chemical equilibrium. The distribution between the bimetallic compounds can be altered by varying the cyanide concentration (e.g. by changing the pH), and/or by changing the Pt/Tl ratio. An excess of cyanide shifts equilibria 4 and 8 from the Pt-Tl complexes to mononuclear platinum and thallium cyano species. The high values of stability constants calculated for the bimetallic complexes **I−V** imply thermodynamically favourable formation of both the metal−metal bond and the $(CN)_5Pt-$ unit; the latter can be considered to be a ligand coordinated to thallium. Comparison of the stepwise stability constants for $[(CN)_5Pt-Tl(CN)_{n-1}]^{(n-1)-}$ complexes with those for the corresponding parent $Tl(CN)_n^{3-n}$ compounds (cf. Scheme) demonstrates the strong influence of the platinum cyano unit resulting in a substantial weakening of the Tl−C bonds.

It is very unusual that equilibria are reported for metal−metal bonded compounds and, according to our knowledge, the present work constitutes the first detailed equilibrium study of such a system. These results suggest that many of the reactions resulting in cluster formation are real equilibria (although many can be dominantly shifted to one direction) and that they can be studied using the tools of equilibrium coordination chemistry. Further work is certainly required to confirm if this observation applies to other cluster formation reactions which have been reported in the literature.

Supplementary Material

Data of the equilibrium study (tables of titration data from 6 independent potentiometric and NMR titrations and a serial dilution) can be obtained from the authors.

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Experimental Section

Materials: A concentrated (1.45 M) aqueous solution of $Tl(ClO_4)_3$ in 3.77 M $HClO_4$ was obtained by anodic oxidation of $TlClO_4$.[16] Solutions of thallium(III) cyanide complexes were synthesised by addition of a calculated volume of a sodium cyanide solution (and NaOH when needed) to the stock solution of thallium(III) perchlorate. Potassium tetracyanoplatinate(II) trihydrate (Aldrich, reagent grade) was used without further purification. The solution of sodium tetracyanoplatinate(II) was prepared by precipitation of potassium perchlorate from the aqueous solution of $K_2Pt(CN)_4$ with an excess of aqueous sodium perchlorate at 275 K and was used as a stock platinum solution.

Equilibrium Studies: All the solutions were kept dark to avoid photochemical decomposition. Samples were prepared by mixing the solutions of $Na_2Pt(CN)_4$ and $Tl(CN)_2^+$ both containing 1 M $NaClO_4$ as ionic medium, and the solutions were kept at room temperature overnight prior to titrations. The complex, $Tl(CN)_2^+$, was prepared from thallium(III) perchlorate (1.45 mol/l Tl^{3+} and 3.77 mol/l H^+) and sodium cyanide solutions (molar ratio CN/Tl = 3) which resulted in exclusive formation of $Tl(CN)_2^+$ species (at the actual pH value). 2.00-ml samples containing $[Tl]_{tot}$ = 54.0 mM, $[Pt]_{tot}$ = 49.8 mM, $[CN]_{tot}$ = 334 mM, were titrated with an aqueous solution of: (titration A) 3.32 M $HClO_4$ (starting pH 4.7) or (titration B) 3.5 M NaCN (starting pH 3.6). In a different experiment, 2.26 ml sample with $[Tl]_{tot}$ = 44.3 mM, $[Pt]_{tot}$ = 57.5 mM, $[CN]_{tot}$ = 341 mM, $[HClO_4]$ = 382 mM was titrated with 3.5 M NaCN (titration C) (see Supplementary Material).

The titrations were performed by using a syringe to add aliquotes of the titrant (5−100 µl) into the NMR tube through a rubber seal, and subsequently recording ^{205}Tl-NMR spectra to measure the signal integrals of the Tl^{III}-containing species and Tl^+. Tl^+ was present as a contaminant in the thallium(III) stock solution and as a product of the slow, but not negligible redox reaction due to the some unavoidable exposure to light. Nevertheless, the Tl^+ content never exceeded 15% of the total thallium concentration.[1][17]

In order to study the formation of the trinuclear complex samples (titration D) were prepared where the Pt/Tl ratio was 2. D1−D5: pH = 1.7±0.2, $[Tl]_{tot}$ = 40.0 mM, 30.0 mM, 20 mM, 15 mM, and 10 mM; $[Pt]_{tot}$ = 2 $[Tl]_{tot}$, $[CN]_{tot}$ = 11 $[Tl]_{tot}$, respectively. ^{205}Tl-NMR spectra were recorded as for the titrations mentioned above, and the $[Pt(CN)_4^{2-}]$ was also measured by integration of the ^{205}Pt-NMR signal. Since the individual species were in the slow exchange regime on the actual ^{205}Tl- and ^{205}Pt-NMR time scales, the signal integrals could be measured and the mole ratios calculated.

In order to measure $[H^+]$, the samples identical to A, B, and C were used to measure the pH by potentiometric titrations. pH values were measured by a combination electrode connected to a pH-meter (Radiometer PHM93). The readings of the electrode were calibrated to pH values using the method of Irving for pH > 1,[18] and by direct determination for pH < 1. These data resulted in *stoichiometric stability constants.*

NMR Measurements: NMR spectra were recorded with Bruker AM400 and Bruker DMX500 spectrometers at a probe temperature of 298 (±0.5) K. The following, typical NMR parameters were used:

^{205}Tl NMR: (AM400) spectrometer frequency (SF) = 230.8 MHz; spectral window (SW) = 50 kHz; pulse width (PW) = 7 µs (flip angle ca. 30°); pulse repetition time 2.16 s; digital resolution 12 Hz/point; and number of scans = 200−1000; (DMX500) SF = 288.49 MHz; SW = 7.2 kHz; pulse width (p1) = 9.6 µs (flip angle 90^0); pulse repetition time 5.33 s; digital resolution 18 Hz/point; number of scans 500. The chemical shifts are referred in ppm toward higher frequency from the ^{205}Tl-NMR signal of an aqueous solution of $TlClO_4$, extrapolated to infinite dilution. The transmitter frequency (O1) was positioned at the resonance of the ^{205}Tl nuclei uncoupled to ^{195}Pt and the intensity of this signal was measured directly from the spectra. In the equilibrium study, the sum of the integrals (in the absolute intensity mode) measured at different points of the NMR titration was not constant because the 90° pulse varied with the acidity of the sample resulting in a non-equal excitation of the signals. This was, however, not a problem since the total concentration of thallium in the titrated solution was known throughout the titration. Aqueous solutions of 25 and 50 mM $TlClO_4$ in 1 M $NaClO_4$ were used to calibrate the signal integrals. The accuracy of the integrals was estimated to 3−5%.

^{195}Pt NMR: (AM400) SF = 85.6 MHz; SW = 50 kHz; PW = 6 µs (flip angle ca. 30°); pulse repetition time 2.16 s; digital resolution 8 Hz/point; number of scans = 1000−10000; (DMX500) SF = 107.03 MHz; SW = 16 kHz ; P(90^0) = 13.0 µs (flip angle 90^0); pulse repetition time 1.3 s; digital resolution 17 Hz/point; number of scans 1500. The chemical shifts were measured relative to an external standard of aqueous 0.1 M Na_2PtCl_6 which is 4533 ppm

to higher frequency from $\Xi(^{195}Pt) = 21.4$ MHz at 25 ^{0}C.[19] A 15.0 mM aqueous solution of $K_2Pt(CN)_4$ was used for calibration of intensities of signals when measuring quantitative integrals. The accuracy of the integrals was estimated to 3−5%.

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