Nonbuttressed Metal−Metal-Bonded Complexes of Platinum and Thallium in Aqueous Solution: Characterization of $[(NC)_5Pt-Tl(CN)]^-$ by Multinuclear NMR

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Recently, considerable interest has been devoted to the synthesis of so-called "light-harvesting" compounds. These compounds should by thermodynamically stable and undergo photochemically induced reversible redox-reactions when exposed to daylight. An example of this type of compound is the cyanide-bridged complex ion $[(NC)_5Fe^{II}-CN-Pt^{IV}(NH_3)_4-NC-Fe^{II}(CN)_5]^{4-}$, prepared by Bocarsly *et al.*[1] The starting point of the present study was a synthesis of oligometallic compounds where a simultaneous two-electron transfer between two metal centers could be anticipated. We selected platinum and thallium because of their ability to form a variety of strong complexes, thus providing opportunities to tune their redox potentials and reaction kinetics. During our studies of some heterobinuclear compounds we have discovered a family of complexes containing nonbuttressed Pt−Tl metal−metal bonds which are surprisingly stable in aqueous solution.

This communication describes the formation and characterization of the first of this new class of complexes, namely, the photochemically active complex ion $[(NC)_5Pt-Tl(CN)]^-$. Under certain conditions this binuclear species slowly decomposes yielding Tl(I) and the hitherto unknown $[Pt^{IV}(CN)_5(OH_2)]^-$ ion. The reaction stoichiometry is described in Scheme 1.

Scheme 1

$$[Pt^{II}(CN)_4]^{2-} + \text{“}[Tl^{III}(CN)_3]\text{”} + H^+ \rightleftharpoons [(NC)_5Pt-Tl(CN)]^- + HCN \qquad \text{formation}$$

$$[(NC)_5Pt-Tl(CN)]^- + H_2O + H^+ \overset{h\nu}{\rightleftharpoons} [Pt^{IV}(CN)_5(OH_2)]^- + Tl^+ + HCN \qquad \text{decomposition}$$

$$[Pt^{IV}(CN)_5(OH_2)]^- + HCN \rightleftharpoons [Pt^{IV}(CN)_6]^{2-} + H_2O + H^+ \qquad \text{equilibration}$$

The Pt−Tl species appear during the oxidation of Pt(II) to Pt(IV) by Tl(III), which in turn is reduced to Tl(I). In the course of the reaction between equimolar aqueous solutions of "$Tl^{III}(CN)_3$"[2] and the complex ion $[Pt^{II}(CN)_4]^{2-}$[3] a range of binuclear Pt−Tl species are successively formed. The NMR data for the binuclear species are summarized in Table 1.

At room temperature and exposed to daylight in acidic solution (pH ≈ 2) the reaction giving mononuclear Pt(IV) and Tl(I) is completed after 3−4 days. However, if the solution is stored in the dark at 8 °C, the major Pt−Tl complex **II**, having $^1J(^{195}Pt-^{205}Tl) \approx 57$ kHz, is found to be stable over a period of at least 6 months and has been characterized by multinuclear NMR[4] and Raman spectroscopy. Complexes **III** and **IV** are currently under study.

Table 1. NMR Data (25 °C) for the Binuclear Pt−Tl Compounds[a] and Some Other Species Formed during the Reaction between Aqueous Solutions of "$[Tl^{III}(CN)_3]$" and $[Pt^{II}(CN)_4]^{2-}$ [b]

species	$J(^{195}Pt-^{205}Tl)$/kHz[c]	δ ^{205}Tl/ppm[5]	δ ^{195}Pt/ppm[9]
$[Tl^{III}(CN)_2]^+$		2411(2)[d]	
$[Tl^{III}(CN)_3]$		2842(2)[e]	
$[Pt^{II}(CN)_4]^{2-}$			−220[f]
Pt−Tl (intermediate)	25.4(1)	1243(1)	576(2)[g]
Pt−Tl **II**	57.0(1)	1377(1)	369(2)[g,h]
Pt−Tl **III**	48.1(1)	1975(1)	175(2)[g]
Pt−Tl **IV**	38.9(1)	2224(1)	65(2)
Tl^+		−59(1)	
$[Pt^{IV}(CN)_5(OH_2)]^-$			1233(2)
$[Pt^{IV}(CN)_6]^{2-}$			646(2)

[a] The Pt−Tl species are denoted **II**−**IV** depending on their order of appearance during the course of the studied reaction, where the intermediate (lifetime ~ 1 day) and **II** are the first complexes formed. [b] Estimated experimental uncertainties are given in parentheses. [c] The coupling constants are a mean value from ^{205}Tl and ^{195}Pt NMR for solutions with varying compositions. [d] $\delta_C = 142(1)$ ppm. [e] $\delta_C = 147(1)$ ppm. [f] $\delta_C = 128(1)$ ppm, $^1J(^{13}C-^{195}Pt) = 1031(3)$ Hz. [g] Recorded at 15 °C. [h] $\delta_{Pt} = 375(2)$ ppm at 25 °C.

The spin−spin coupling patterns in the ^{205}Tl NMR spectra[5] of complexes **II**−**IV** and the intermediate confirm that these species are indeed heterobinuclear. The ^{205}Tl NMR signal of each complex is first split into a 1:1 doublet by coupling to *one* ^{195}Pt nucleus ($I = {}^1/_2$, natural abundance 33.8%). The one-bond coupling constants between ^{205}Tl and ^{195}Pt nuclei are given in Table 1. Due to the presence of several nonmagnetic isotopes of platinum which do not couple to ^{205}Tl, a central peak is superimposed on the doublet, resulting in triplets with the expected intensity ratio 1:3.9:1.

To obtain more detailed structural information about complex **II**, starting solutions of "$[Tl^{III}(CN)_3]$" and $[Pt^{II}(CN)_4]^{2-}$ were 100% enriched using $Na^{13}CN$.[6] The coupling pattern in the ^{205}Tl NMR spectra of the ^{13}C-enriched solution was assigned in terms of an AMX_4 spin system for the carbon sites (Figure 1). This indicates that **II** contains a total of six cyanide ligands, of which four are chemically equivalent. For discussion purposes the three cyanides are denoted C^A, C^B, and C^C with spin−spin coupling constants (kHz) $J(^{205}Tl-^{13}C^A) = 9.71$, $J(^{205}Tl-^{13}C^B) = 2.44$, and $J(^{205}Tl-^{13}C^C) = 0.45$, respectively.

The ^{13}C NMR spectra[7] of solutions containing **II** (Figure 2) are fully compatible with the ^{205}Tl NMR. Signals for the three cyanide sites are observed at $\delta_{C^A} = 99$ ppm, $\delta_{C^B} = 162$ ppm, and $\delta_{C^C} = 88$ ppm, respectively, with the expected intensity ratio 1:1:4. Besides spin−spin coupling to ^{205}Tl as described above, all three cyanide carbons are coupled to the ^{195}Pt center in **II**, where $J(^{13}C^A-^{195}Pt) = 0.84$ kHz, $J(^{13}C^B-^{195}Pt) = 0.20$ kHz, and $J(^{13}C^C-^{195}Pt) = 0.83$ kHz. Moreover, C^A and C^B couple to each other, resulting in doublets with $^3J = 30(2)$ Hz. The 1:1 doublet at $\delta_C = 115$ ppm in Figure 2 is due to $H^{13}CN$.[8]

The platinum NMR spectrum[9] consists essentially of a 1:1 doublet due to coupling between the ^{195}Pt and ^{205}Tl nuclei in **II** (for ^{205}Tl, $I = {}^1/_2$, natural abundance 70.5%); see Table 1. A second 1:1 doublet is also observed due to coupling to the ^{203}Tl nucleus ($I = {}^1/_2$, natural abundance 29.5%). In addition, each of these peaks is seemingly split into a sextet. This can be explained by similar Pt−C coupling constants for C^A and

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(1) Pfennig, B. W.; Bocarsly, A. B. *Inorg. Chem.* **1991**, *30*, 666.

(2) The solution of "$[Tl(CN)_3]$" was prepared by adding 3 equiv of NaCN(s) to a concentrated solution of $Tl(ClO_4)_3$ in perchloric acid ($[Tl^{3+}] = 1.45$ M, $[H^+] = 3.77$ M) obtained by anodic oxidation of Tl(I).[24] The "$[Tl(CN)_3]$" solution contains the complexes $Tl(CN)_2^+$ (85% of the total Tl^{III}) and $Tl(CN)_3$ (15%), as determined from the ^{205}Tl spectra.

(3) Solid $K_2Pt(CN)_4 \cdot 3H_2O$ (Aldrich) was dissolved in water and the potassium precipitated as $KClO_4$(s) by the addition of 3.0 M $HClO_4$ (aqueous). The solution contained only one platinum species, $Pt(CN)_4^{2-}$, as determined by ^{195}Pt NMR.

(4) All ^{205}Tl, ^{195}Pt, and ^{13}C spectra have been recorded at 230.8, 85.6, and 100.6 MHz, respectively, on a Bruker AM400 spectrometer.

(5) Given in ppm toward higher frequency with respect to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution at 25 °C.

(6) K_2PtCl_4 (aqueous) and $Na^{13}CN$(s) (Merck) were used in the preparation of ^{13}C-enriched $K_2Pt(^{13}CN)_4 \cdot nH_2O$(s) crystals and also for the "$[Tl(^{13}CN)_3]$" solution, which were used to prepare an acidic equimolar solution of Tl(III) and Pt(II) cyanide. The composition of this sample was (mM) $[Tl^{3+}] = 50$, $[Pt(^{13}CN)_4{}^{2-}] = 51$, $[^{13}CN^-] = 148$, and $[H^+] = 53$.

(7) Given in ppm toward higher frequency with respect to TMS* at 25 °C.

(8) Bányai, I.; Blixt, J.; Glaser, J.; Tóth, I. *Acta Chem. Scand.* **1992**, *46*, 142.

(9) Given in ppm toward higher frequency from $\Xi(^{195}Pt) = 21.4$ MHz. $\delta[PtCl_4]^{2-} = 2896$ ppm (in H_2O at 25 °C).

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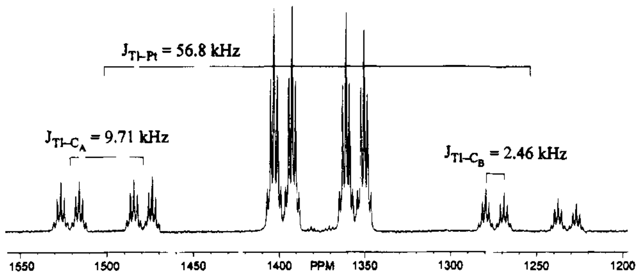


Figure 1. ^{205}Tl NMR spectrum (recorded at 25 °C) of the 100% ^{13}C enriched Pt−Tl complex **II** (see text).

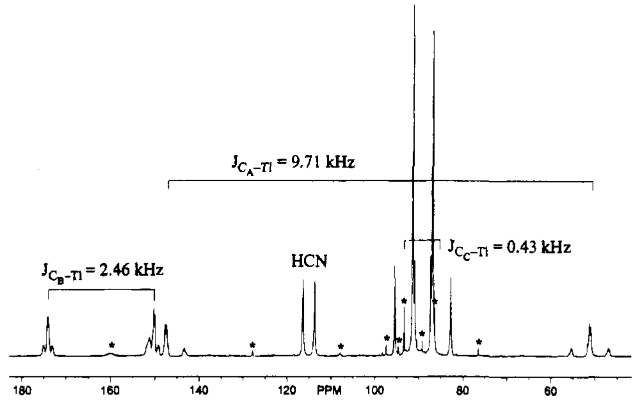


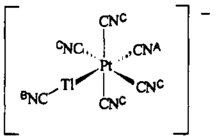
Figure 2. ^{13}C NMR spectrum (25 °C) of the 100% ^{13}C enriched Pt−Tl complex **II**, showing the three different cyanide carbons (C^A, C^B, and C^C) in **II**. ^{13}C signals for some minor monomeric Pt and Tl cyanide species in the solution are marked with an asterisk (see text).

C^C (see above). Furthermore, the sextet is split into doublets by C^B, where $J(^{195}\text{Pt}-^{13}\text{C}^B) = 0.20$ kHz.

An interesting product that forms during the decomposition of **II** according to Scheme 1 is the hitherto unknown ion $[\text{Pt}^{IV}(\text{CN})_5(\text{OH}_2)]^-$. In ^{13}C NMR, each signal appears as a three-line pattern as described above ($^1J_{\text{Pt}-cis\text{-C}} = 823(3)$ Hz, $^1J_{\text{Pt}-trans\text{-C}} = 1025(3)$ Hz). The signal for the four chemically equivalent *cis* carbons, $\delta_C = 95(1)$ ppm, is further split by the *trans* carbon into doublets ($^2J_{cis\text{-C}-trans\text{-C}} = 4.6(2)$ Hz). Three pentets (1:3.9:1) were observed for the carbon *trans* to H_2O, $\delta_C = 76(1)$ ppm. In ^{195}Pt NMR, the signal for $[\text{Pt}^{IV}(\text{CN})_5(\text{OH}_2)]^-$ is observed at 1233(2) ppm (Table 1). The formation of this kinetically inert[10] complex and its slow reaction with free CN$^-$ to form $[\text{Pt(CN)}_6]^{2-}$ are compatible with the fact that a Pt(CN)_5 entity is present in the proposed structure of the Pt−Tl compound **II**.

We conclude that complex **II** is heteronuclear in aqueous solution, with one Pt and one Tl center, and contains six cyanide ligands of which four are chemically (and magnetically) equivalent with pseudo-square-planar coordination around platinum. The platinum and thallium centers are linked by a metal−metal bond with no buttressing ligands.

II



The C^A and C^B carbons in complex **II** could be assigned on the basis of ^{13}C and ^{195}Pt spectra. The carbon C^A, with a chemical shift typical for platinum cyanides[11] and a Pt−C^A coupling constant similar to that of Pt−C^C, coordinates directly to the platinum center. C^A couples strongly to the two Tl isotopes; the separation between the ^{13}C^A (^{205}Tl) and ^{13}C^A (^{203}Tl) signals is 45(2) Hz, as expected for the Tl−C^A coupling constant of almost ≈10 kHz. A corresponding but smaller separation is expected for C^B. The difference in frequency between the two Tl isotopes is almost the same as the actual C^A−C^B coupling constant ($J = 30(2)$ Hz). Hence, only a slight asymmetry of the peaks is observed for C^B (Figure 2). The Tl−C^B coupling constant of 2.44 kHz indicates that the oxidation state of thallium is higher than +1,[12,13] which is unprecedented for Pt−Tl complexes.[14−16]

The ^{195}Pt−^{205}Tl coupling constant for the heterobinuclear species **II** is the largest known between two *different* nuclei, larger than, e.g., $^1J(^{195}\text{Pt}-^{119}\text{Sn})$ in $[\text{Pt(SnCl}_3)_n\text{X}]$.[17,18] This is due to the large magnetogyric ratio of the ^{205}Tl nucleus and the pronounced s-character[19] and strength of the Pt−Tl bond. The Pt−Tl stretching band at $\nu = 161$ cm^{-1} in the Raman spectrum of **II** in aqueous solution is also indicative of a strong metal−metal bond.[20]

Direct metal−metal bonding is normally observed in the solid state, and such compounds containing platinum and thallium have previously been synthesized.[14−16] All previously obtained Tl compounds contain thallium in the +1 oxidation state, which is not the case in complex **II** as judged from the large Tl−C^{B}N coupling constant.[13] The narrow NMR signals indicate that the complex is diamagnetic. Thus, the *formal* oxidation states can be Pt^{II}−Tl^{III}, or Pt^{III}−Tl^{II} with an electron pair localized in a σ-bond between the metal centers (cf. the ligand-supported Rh^{II}−Rh^{II} [21] and Pt^{III}−Pt^{III} [22] compounds). Usually, metal NMR chemical shifts are very sensitive to the metal oxidation state. The ^{205}Tl NMR chemical shift of **II**, 1337 ppm, is far outside the Tl^I region (−200 to +200 ppm)[23] and much lower than the chemical shifts of the Tl^{III} cyano complexes (+2000 to +3000 ppm).[12] Moreover, the ^{195}Pt NMR shift of **II** is between the chemical shift regions of Pt^{II} and Pt^{IV} cyano complexes (cf. Table 1). This data, together with the Pt−Tl Raman frequency, indicates that **II** contains a single-bonded Pt−Tl couple with a shared electron pair.

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Supporting Information Available: Expansions of multinuclear NMR spectra (^{13}C, ^{195}Pt, ^{205}Tl) of the studied solutions (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) Tl^I does not form complexes with CN$^-$,[25] whereas the complexes $\text{Tl}^{III}(\text{CN})_n{}^{3-n}$ are very strong, with Tl−C coupling constants varying in the range 5−15 kHz.[12]

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