New Class of Oligonuclear Platinum−Thallium Compounds with a Direct Metal−Metal Bond. 2. Structural Characterization of the Complexes

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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. The structure of these compounds represented by the formula $[(NC)_5Pt-Tl(CN)_{n-1}]^{(n-1)-}$ ($n = 1-4$ for compound **I**, **II**, **III**, and **IV**, respectively) was determined by means of multinuclear NMR (^{195}Pt, ^{205}Tl, ^{13}C) supported by Raman spectroscopy. In addition, a trinuclear complex with the formula $[(NC)_5Pt-Tl-Pt(CN)_5]^{3-}$ is formed in solutions where the Pt/Tl ratio is larger than 1. The compounds exhibit very large one-bond ^{195}Pt−^{205}Tl spin−spin coupling constants, 25−71 kHz; the value for compound **I**, 71 060 Hz, is the largest reported coupling constant between two different nuclei. The possible reasons for this strong coupling, as well as its variation along the series of the binuclear compounds **I**−**IV**, are discussed in terms of the metal−metal bond strength, varying participation of s-electrons in this bond and oxidation state of the metal ions.

Introduction

The interest in direct metal−metal linkage between platinum and thallium atoms was initiated by Nagle and Balch, who reported six-coordinated platinum in the structure of *trans*-$Tl_2Pt(CN)_4$ which does not possess the usual for platinum(II) tetracyano salts Pt−Pt linked columnar structure but involves two covalent Pt−Tl bonds.[1] The unusual structure and strong luminescence exhibited by this compound initiated several studies of its electronic properties.[2−4] Later, a Pt−Tl bond was also found in such compounds as the binuclear $[Tl(crown\text{-}P_2)Pt(CN)_2](NO_3)$[5] and in two trinuclear Pt−Tl−Pt species: *cis*-$[Tl\{(1\text{-}MeT)_2Pt(NH_3)_2\}_2](NO_3)\cdot 7H_2O$[6] and $(NBu_4)_2[Tl\{Pt(C_6F_5)_4\}_2]$.[7] The oxidation state of platinum is +2 in all these compounds. Thallium is monovalent in these compounds except the latter one, in which the oxidation state is +2: the presence of an unpaired electron makes the compound paramagnetic. Three compounds containing a $TlPt_3$ cluster unit have also been prepared: $[TlPt_3(CO)_3(PCy_3)_3][Rh(\eta\text{-}C_8H_{12})Cl_2]$,[8] $[TlPt_6(\mu\text{-}CO)_6(\mu\text{-}dppp)_3]^+$,[9] and $[Pt_3\{\mu_3-Tl(acac)\}(ReO_3)(\mu\text{-}dppm)_3]^+$.[10] The latter compounds contain zerovalent platinum and monovalent thallium. Previous attempts to react Pt^{II} and Tl^{III} entities have not resulted in formation of a direct metal−metal bond between these two atoms.[11]

It can be noted that all metal−metal-bonded compounds mentioned above have been prepared in the solid state and are normally not stable in solution, especially not in water. Recently, we have shortly described the formation and characterization of the first representative of a new class of Pt−Tl cyanide species containing a strong unsupported metal−metal bond, namely, the complex ion $[(NC)_5Pt-Tl(CN)]^-$ which is formed in aqueous solution by the reaction between Pt^{II} and Tl^{III} cyano complexes.[12] Here we report a detailed structural study of a whole family of bimetallic cyano compounds obtained in the $Pt^{2+}-Tl^{3+}-CN^--H_2O$ system in solution and characterized by multinuclear NMR and Raman spectroscopy.

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 $TlClO_4$.[13] A concentrated acidic solution of $Tl(NO_3)_3$ (1.42 M in 2.96 M HNO_3) was prepared by direct dissolution of thallium(III) oxide in nitric acid under heating. Solutions of thallium(III) cyanide complexes were synthesized either by the method described previously[14] or by a direct dissolution of Tl_2O_3 in hydrocyanic acid.[15] Depending on the synthetic route, the content of Tl^I in the starting thallium solution varied from 1 to 5% of the total thallium concentration. Potassium tetracyanoplatinate(II) trihydrate (Aldrich, reagent grade) was used without further

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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. For some NMR measurements ^{13}C-enriched solutions (99%) were used; in this case $Tl^{III}(^{13}CN)_n^{3-n}$ species were prepared using $Na^{13}CN$ salt, whereas $Na_2Pt(^{13}CN)_4$ salt was obtained from the exchange reaction between K_2PtCl_4 and $Na^{13}CN$ in aqueous solution with molar ratio $^{13}CN/Pt = 6$, followed by recrystallization of the tetracyanoplatinate salt. Calcd for $Na_2Pt(^{13}CN)_4 \cdot H_2O$: Pt, 53.1; Na, 12.5. Found: Pt, 54.4; Na, 12.6.

Solutions of Pt−Tl−CN Complexes. Bimetallic Pt−Tl cyano complexes in aqueous solution were prepared by mixing solutions of $Pt(CN)_4^{2-}$ and $Tl(CN)_n^{3-n}$ ($n = 2-4$) species at different metal to metal and cyanide-to-metal ratios. The solutions were kept dark to avoid photochemical decomposition.[16]

^{13}C-enriched bimetallic Pt−Tl cyano compounds were obtained when the starting solutions of $Pt(CN)_4^{2-}$ and $Tl(CN)_2^+$ were 99% enriched using $Na^{13}CN$. After mixing, the resulting $Pt(^{13}CN)_4^{2-}-Tl(^{13}CN)_2^+$ solution with the ratio Pt/Tl = 1:1 was divided into two portions which were titrated (a) with 1.20 M solution of $Na^{13}CN$ or (b) with 3.32 M $HClO_4$ in order to decrease the concentration of free CN^-. This procedure allowed us to cover all soluble binuclear Pt−Tl species, and the recorded ^{205}Tl, ^{195}Pt, and ^{13}C NMR data were sufficient for the determination of their structures. For the study of the trinuclear Pt−Tl−Pt complex the same solutions of ^{13}C-enriched thallium and platinum cyanides were mixed with the ratio Pt/Tl = 2:1.

A technique of partial ^{13}C enrichment was also very helpful for spectral assignment. It was found that the cyano ligands of $Pt(CN)_4^{2-}$ are sufficiently inert with respect to the ligand exchange with the thallium site. This fact allowed preparation of the Pt−Tl compounds by the reaction between $Pt(^{12}CN)_4^{2-}$ and $Tl(^{13}CN)_2^+$ (or between $Pt(^{13}CN)_4^{2-}$ and $Tl(^{12}CN)_2^+$). In the current work this method was used only for the structural assignment of the trinuclear Pt−Tl−Pt complex.

Analysis. The analytical methods for determination of the H^+, Tl^{3+}, and Tl^+ concentrations in the solutions were described previously.[14] 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,[17] and by direct calibration for pH < 1.

NMR Measurements. All NMR spectra were recorded with a Bruker AM400 spectrometer at a probe temperature of 298(±0.5) K. Typical NMR parameters for obtaining ^{205}Tl, ^{195}Pt, and ^{13}C spectra were presented in our recent publications.[12,14] The chemical shifts were referred (in ppm) toward higher frequency from signals of (a) aqueous solution of $TlClO_4$, extrapolated to infinite dilution, (b) aqueous 0.1 M Na_2PtCl_6 (4533 ppm to higher frequency from $X(^{195}Pt) = 21.4$ MHz at 25 °C), and (c) water-soluble sodium salt of TMS, for ^{205}Tl, ^{195}Pt, and ^{13}C NMR spectra, respectively.

Raman Spectroscopy. Raman spectra were excited using premonochromatized 514.5 nm radiation from a Coherent Radiation Laboratories Innova 90-5 argon ion laser at an effective power of approximately 400 mW at the sample. Solution spectra from typically 0.05−0.1 M aqueous solutions in glass cuvettes were recorded by means of Dilor Z24 triple monochromator at a spectral bandwidth of 4 cm^{-1} using photon counting.

Results

A. Characterization of Pt−Tl Cyano Complexes in Aqueous Solution by Multinuclear NMR. (1). Formation of Pt−Tl Species.

Reaction between colorless aqueous solutions of $Pt(CN)_4^{2-}$ and thallium(III) perchlorate or nitrate (with Pt/Tl molar ratio 1:1) results in an immediate and practically quantitative precipitation of a yellow powder. The only species which could be detected (in small amounts) by ^{195}Pt and ^{205}Tl NMR spectra of the mother liquor after filtration of the precipitate were either $Pt(CN)_4^{2-}$ ($\delta = -214$ ppm) or Tl_{aq}^{3+} ($\delta = 2034$ ppm), indicating a small excess of either platinum or thallium in the starting solutions.

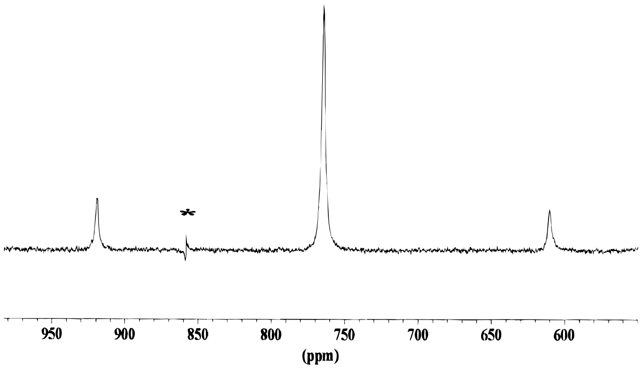

Figure 1. ^{205}Tl NMR spectrum of complex **I** in an aqueous solution containing 50 mM Tl^{3+} (added as nitrate solution), 50 mM $Pt(CN)_4^{2-}$ (added as potassium solution), and 100 mM KCN at pH 0.34. The asterisk denotes the back-folded signal of complex **II**.

Addition of ionic cyanide (aqueous solution of NaCN) to the systems results in an increase of solubility of the precipitate which dissolves completely at a molar ratio $[CN]_{tot}/M \geq 6$ (M = Pt, or Tl), indicating further coordination of the CN^- ligands to the metal ions. Dissolution of the powders is accompanied by appearance in ^{205}Tl NMR spectra of two new groups of triplet signals (with intensity ratio 1:4:1) centered at about 780 (the shift differs slightly from that in nitrate medium) and 1370 ppm and assigned to complexes **I** and **II**, respectively (Figure 1 and Table 1). The two small peaks in each triplet arise from the spin−spin coupling between the ^{205}Tl and ^{195}Pt nuclei (^{195}Pt: $I = {}^1/_2$, natural abundance 33.8%), and together with the central uncoupled peak they give the intensity ratio of 1:3.9:1 as expected for thallium bonding with one platinum atom in the species. The coupling constants $J(^{205}Tl-^{195}Pt)$ are ~71 and ~57 kHz for **I** and **II**, respectively. The same values of coupling constants were obtained from ^{195}Pt NMR spectra of these solutions. The latter spectra consist of two pairs of 1:1 doublets, with the ratio of approximately 2.4 between them, due to coupling to the two isotopomers of thallium (^{205}Tl and ^{203}Tl both have $I = {}^1/_2$, natural abundance 70.5% and 29.5%, respectively) and are centered at 473 and 383 ppm for **I** and **II** (cf. Figure 2), respectively. Along with ^{205}Tl NMR data, this shows that the complexes are heterobinuclear.[18]

Upon further addition of the cyanide ion to the $Pt(CN)_4^{2-}-Tl(CN)_2^+-H_2O$ system ($[CN]_{tot}/M > 6$), ^{205}Tl NMR signals (1:4:1 triplets) of two additional platinum−thallium complexes appear in the spectra. The signals are centered at 1975 (**III**) and 2224 ppm (**IV**), and the $^{195}Pt-^{205}Tl$ coupling constants are ~47 and ~38 kHz, respectively. These complexes are also binuclear: in ^{195}Pt NMR spectra they appear as pairs of doublets centered at 184 (**III**) and 68 (**IV**) ppm with the same values of coupling constants as those obtained from ^{205}Tl NMR (Table 1). The same result was obtained when $Tl(CN)_3$ (yields compound **III**) or $Tl(CN)_4^-$ (yields compound **IV**) was used as a starting complex for the reaction with tetracyanoplatinate.

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[16] (a) In the previous paper[12] we have shown that when the oligonuclear Pt−Tl compounds are exposed to light electron transfer is initiated between the two metal atoms, leading to dissociation of the metal−metal bond. The only thallium product of this redox reaction is Tl^+, whereas the oxidation of platinum results in formation of mononuclear cyano complexes of Pt(IV) and a Pt(III) cyano dimer.[16b] (b) Maliarik, M.; Glaser, J.; Tóth, I. *Inorg. Chem.*, submitted for publication.

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[18] The complexes **I** and **II** are also formed when reaction is carried out between solutions of $Pt(CN)_4^{2-}$ and $Tl(CN)_2^+$ with the molar ratio Pt:Tl = 1:1.

Table 1. NMR Parameters for Pt−Tl−CN Compounds and Some Related Platinum and Thallium Species in Aqueous Solution[a,b]

species	δ_{Tl}	δ_{Pt}	δ_{C^A}	δ_{C^B}/m^c	δ_{C^C}	$^1J_{Tl-Pt}$	$^2J_{Tl-C^A}$	$^1J_{Tl-C^B}$	$^2J_{Tl-C^C}$	$^1J_{Pt-C^A}$	$^2J_{Pt-C^B}$	$^1J_{Pt-C^C}$	$^3J_{C^A-C^B}$
Tl^I/[d]	0		–	–		–	–	–	–	–	–		–
$Pt^{IV}(CN)_6^{2-}$		655			88.8							806	
I	786	473	93.4	–/0	90.3	71060	12746	–	592	909	–	820	–
II	1371	383	101.7	164.8/1	91.1	57020	9743	2446	452	843	200	821	30
III	1975	184	110.6	156.9/2	93.4	47260	8446	876[e]	338	783	128	832	19
IV	2224	68	116.1	141.9/3[f]	97.0	38760	7270	52[e]	255	742	~0	843	~0
$Tl^{III}(CN)_3$/[g]	2842		–	147.4/3		–	–	7954	–	–	–		–
$Pt^{II}(CN)_4^{2-}$/[g]		−213			130.2							1031	
V	1237	599	117.0	–	95.5	25168	4600	–	308	700 180[h]	–	858	–

[a] All parameters were obtained from the ^{205}Tl, ^{195}Pt, and ^{13}C NMR spectra of the $Pt(^{13}CN)_4^{2-}-Tl(^{13}CN)_2^+$ systems in aqueous solution. [b] The values of spin−spin coupling constants of ^{13}C and ^{195}Pt to ^{203}Tl are not included. [c] *m*, number of cyanides bounded to thallium. [d] Parameters measured in separate solutions of Tl^IClO_4 and $Pt^{IV}(^{13}CN)_6^{2-}$. [e] Values calculated using computer program WIN DAISY. [f] The chemical shift was calculated from the observed exchange averaged signal which results from the exchange between cyanides C^B of **IV** and $Tl(CN)_4^-$, taking into account their content in solution. [g] Parameters measured in separate solutions of $Tl^{III}(^{13}CN)_3$ and $Pt(^{13}CN)_4^{2-}$. [h] $^3J_{Pt-C^A}$.

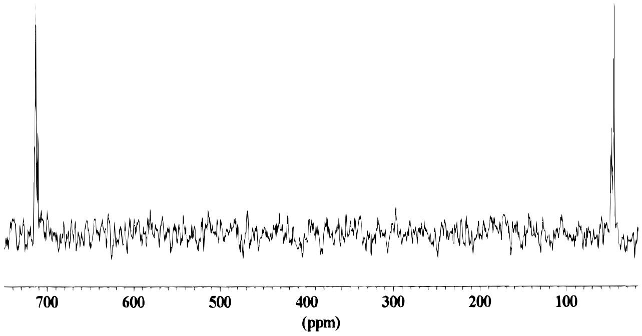

Figure 2. ^{195}Pt NMR spectrum of complex **II** in an aqueous solution containing 50 mM Tl^{3+}, 50 mM Pt^{2+}, and 300 mM $[CN]_{tot}$ at pH 1.08.

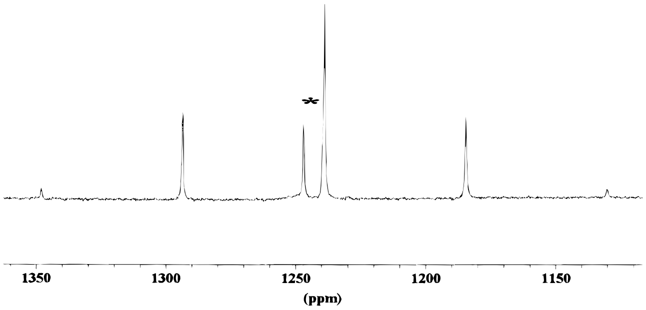

Figure 3. ^{205}Tl NMR spectra of complex **V** in aqueous solutions containing 50 mM Tl^{3+}, 100 mM $Pt(^{12}CN)_4^{2-}$, and 100 mM $Na^{12}CN$; the asterisk denotes the low-frequency part of a signal of complex **II**.

Addition of the ionic cyanide results also in an increase of the basicity of the solution. As a result, for solutions containing **IV** as the dominating binuclear complex, pH is >8 and the anions $Tl(CN)_4^-$ and $Pt(CN)_4^{2-}$ appear in the solution indicating some dissociation of the Pt−Tl species. To study the influence of pH on the bimetallic compounds at constant $[CN]_{tot}$/M ratio, the $Pt(CN)_4^{2-}-Tl(CN)_2^+$ solution was titrated with a 1.0 M solution of sodium hydroxide. Only a small decrease of the concentration of **II** accompanied by an appearance of **III** could be detected, while the concentration of **I** was practically constant in the pH range 0.78−1.58. When pH was further increased, the solution slowly turned brown due to the formation of thallium oxide.

Titration of the $Pt(CN)_4^{2-}-Tl(CN)_2^+$ solution with acid (3.32 M $HClO_4$) has a stronger effect and results in a decrease of the concentration of species **II** accompanied by a smooth increase of the relative concentration of **I**. Thus, at pH = 0.16 up to 50% thallium in the solution is present in the form of complex **I**. At the same time, the decrease of pH causes a precipitation of a white powder, $[(NC)_5PtTl]$,[19] from the solution which restricts the highest available concentration of complex **I** to ~25 mM. A similar effect as for the acid titration was obtained when the $Pt(CN)_4^{2-}-Tl(CN)_2^+$ solution is titrated by an aqueous solution of $AgClO_4$ (1.83 M). Due to the low solubility of AgCN (2.3×10^{-5} g/100 mL at 20 °C) it readily precipitates from the cyanide-containing solutions, allowing a decrease of the concentration of CN^- without significant change of pH; this shifts the equilibrium between the binuclear complexes toward species **I**.[20]

Varying the molar ratio Pt/Tl in the range 1:1−1:4 did not result in the formation of additional Pt−Tl compounds. When an excess of $Tl(CN)_n^{3-n}$ (n = 2−4) was used, the same heteronuclear species were observed as described above, but the amount was limited by the amount of available platinum.

A different situation occurred when tetracyano platinum was added in excess. In $Pt(CN)_4^{2-}-Tl(CN)_2^+$ solutions with Pt/Tl ratio 2:1, a pentet with intensity ratio 1:7.7:17.3:7.7:1 was observed centered at δ_{Tl} = 1237 ppm (Figure 3) (in addition to the triplet signals of complexes **I** and **II**). This intensity distribution almost ideally coincides with the values 1:7.8:17.3:7.8:1 predicted for a ^{205}Tl resonance of a trinuclear Pt−Tl−Pt complex (**V**) considering all possible combinations of magnetic and nonmagnetic Pt nuclei. The value of the ^{205}Tl−^{195}Pt spin−spin coupling constant in this trimer amounts to 25 kHz. ^{195}Pt NMR spectra of this species show two doublets due to coupling of platinum to ^{205}Tl and ^{203}Tl nuclei, centered at 599 ppm (Table 1). No $^2J_{Pt-Pt}$ was observed. Titration of the solution with acid led to a decrease of the concentration of the trinuclear species and, as in the case of binuclear species, the equilibrium shifted toward complex **I**. On the other hand, increasing the concentration of cyanide in the solution resulted in formation of the binuclear complexes **II**−**IV**. Further increase of the platinum concentration in the system (up to Pt/Tl ratio of 4:1) did not result in appearance of additional Pt−Tl species.

Concluding, altogether five oligonuclear Pt−Tl compounds exhibiting strong coupling between the thallium and platinum nuclei were obtained in aqueous solution. The trinuclear Pt−Tl−Pt complex (**V**) could be stabilized in solutions with excess platinum. The formation of the four binuclear Pt−Tl complexes **I**−**IV** (see Table 1) is governed by the cyanide/metal ratio in

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(19) (a) In the solid compound $[(NC)_5PtTl]$ the platinum−thallium separation is 2.63 Å.[19b] (b) Eriksson, L.; Glaser, J., Jalilehvand, F.; Maliarik, M., Persson, I.; Persson, P.; Sandström, M.; Tóth, I. To be published.

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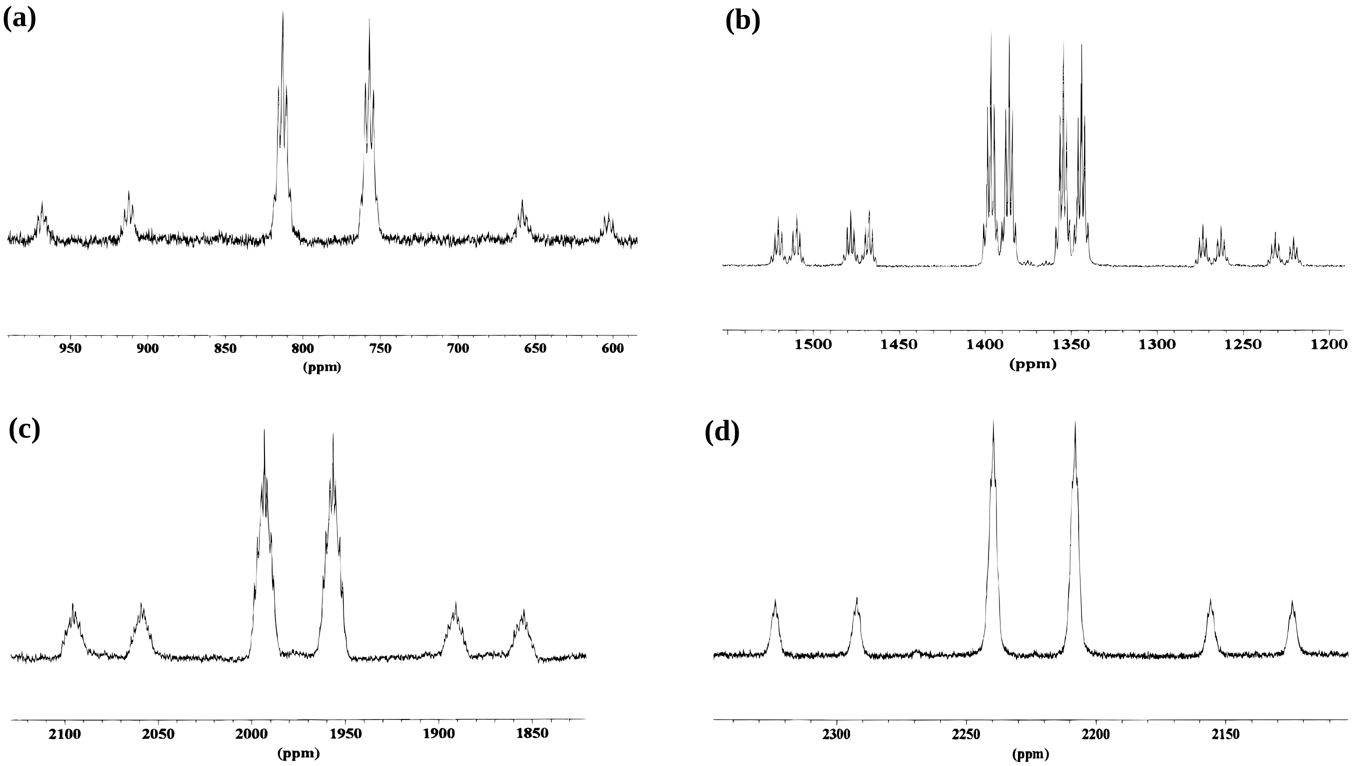
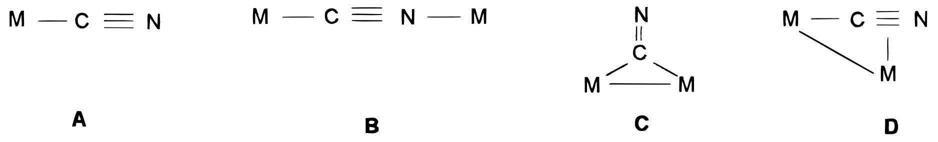


Figure 4. ^{205}Tl NMR spectra of complexes **I**−**IV**, respectively (a−d). Aqueous solution containing 50 mM Tl^{3+}, 50 mM $Pt(^{13}CN)_4^{2-}$, and: 100 mM $Na^{13}CN$ at pH 0.25 (a); 150 mM $Na^{13}CN$ at pH 1.04 (b); 200 mM $Na^{13}CN$ at pH 5.52 (c); 300 mM $Na^{13}CN$ at pH 8.66 (d).

Chart 1



the solution. This indicates that the main difference between these species is the number of cyanide ligands, which strongly influences both ^{195}Pt and ^{205}Tl chemical shifts and the spin−spin coupling constants, $J(^{195}Pt-^{205}Tl)$, of the complexes.

(**2**). **Composition of the Pt−Tl Species and Assignment of the Cyanide Sites. Binuclear Pt−Tl Complexes.** The data for complex **II** were communicated recently.[12] Its ^{205}Tl NMR spectrum (Figure 4b) was assigned in terms of an AMX_4 spin system for the carbon sites. The ^{195}Pt NMR spectrum of the compound is also in agreement with this assignment. Apart from the coupling to the two thallium isotopes, the platinum signal is split into twenty lines present as doublet of doublets of 1:4:6:4:1 pentets, as expected for the coupling to the three groups of nonequivalent carbon-13 nuclei. The three different cyanide types C^A, C^B, and C^C were assigned on the basis of ^{13}C NMR spectra. The four equivalent cyanides, C^C, have both ^{13}C NMR chemical shift and $^1J(^{13}C^C-^{195}Pt)$ values typical for platinum cyano complexes (Table 1). It seems likely that the original coordination geometry of the cyanide ligands in $Pt^{II}(CN)_4^{2-}$ is maintained in **II** and the carbons form a square plane around the platinum atom. The value of the chemical shift for C^B is much closer to those for the $Tl(CN)_n^{3-n}$ complexes than to those for the platinum cyano species (cf. Table 1), but the information from the carbon−metal coupling constants is less conclusive. Still, these data indicate a direct C^B−Tl bonding, whereas the C^B−Pt coupling is probably indirect, through two or more bonds.

The position of the cyanide C^A in the structure of **II** requires some discussion. Its ^{13}C NMR chemical shift and the coupling constant $^1J(^{13}C^A-^{195}Pt)$ are both in the range characteristic for platinum cyanides, which supports its direct bonding to the platinum atom. At the same time this carbon nucleus shows a very strong coupling to ^{205}Tl (∼10 kHz), typical for thallium cyanides and is more than three times larger than $^1J(^{13}C^B-^{205}Tl)$ (Table 1). Moreover, C^A and C^B couple to each other with $J = 30$ Hz, whereas no coupling to C^C can be detected. Several alternatives can be considered for the location of this cyanide ligand, C^A. Four binding modes of cyanide have been reported for binuclear complexes of metal ions. Apart from being coordinated through the carbon at single metal centers (**A**, Chart 1), different types of cyanide bridging between two metal centers as in **B**,[21,22] **C**,[23] or **D**[24,25] are also possible. The formation of structure **B** with a C^A cyanide forming a linear −C≡N− bridge between Pt and Tl atoms is unlikely because of the very strong coupling between ^{195}Pt and ^{205}Tl which indicates that platinum and thallium centers are linked by a direct metal−metal bond. Bridge formation via the C^A carbon atom as in **C** and **D** could both explain the values of $J(^{13}C^A-^{195}Pt)$ and $J(^{13}C^A-^{205}Tl)$ and the strong coupling between the platinum and thallium centers because in this case the metal−metal bond

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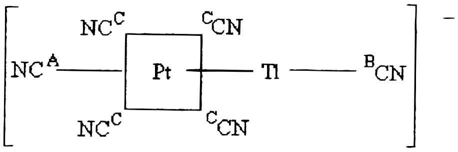
is strengthened by the presence of the bridging group. However, the equivalence of four $\mathrm{C^C}$ cyanides observed in the NMR spectra of all the studied nuclei is not consistent with such a structure, unless there is a rapid rotation of the cyanide around the Pt−Tl bond resulting in both a time-averaged ^{13}C NMR signal of $\mathrm{C^C}$ and a coupling of ^{205}Tl and ^{195}Pt to $\mathrm{C^C}$. Such a rotation would be slowed at lower temperature, and at some stage the nonequivalence of the different cyanides of the $\mathrm{Pt(CN)_4}$ unit would be observed. However, no temperature dependence was observed for the signal of $\mathrm{C^C}$ cyanides in ^{13}C NMR spectra of binuclear Pt−Tl compounds in the range 298−263 K, i.e. down to the freezing temperature of the solution all four carbon nuclei still give one narrow resonance.

Another argument against the presence of bridging cyanide in the structure can be provided by comparison of pairs of coupling constants of $J_{\mathrm{Pt-C^A}}$ and $J_{\mathrm{Pt-C^C}}$, and $J_{\mathrm{Tl-C^A}}$ and $J_{\mathrm{Tl-C^B}}$. Due to the fact that bridging atoms have a higher coordination number than terminal ones it is commonly observed that the magnitudes of ^{1}J(M−L) to bridging ligand atoms (L) are smaller than those to corresponding terminal atoms.[26] For example, in the trinuclear platinum cluster $[\mathrm{Pt_3(Bu^tNC)_6}]$ the values of $^1J_{\mathrm{C-Pt}}$ are 1936 and 357 Hz for terminal and bridging isocyanide ligands, respectively.[27] The spin−spin coupling constants of the platinum atom to the $\mathrm{C^A}$ and to the terminal ($\mathrm{C^C}$) carbons have very similar values, whereas for thallium $J_{\mathrm{Tl-C^A}}$ is several times larger than $J_{\mathrm{Tl-C^B}}$ which lessens the probability that the $^{\mathrm{A}}$CN ligand occupies a bridging position between Pt and Tl centers. It can also be noted that the **C** and **D** types of cyanide bridging have been found only in homonuclear compounds. Therefore, the only plausible location of the cyanide $\mathrm{C^A}$ in the complex is a direct coordination to platinum in a trans position to the thallium atom:

II

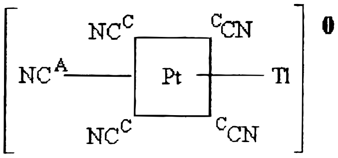


Despite some differences in detail, the general appearance of the ^{195}Pt, ^{205}Tl and ^{13}C NMR spectra is common for all the ^{13}C enriched complexes **I**−**IV** which indicates similar structures of these compounds. The ^{205}Tl NMR spectra are the most informative (Figure 4): in addition to the large spin−spin coupling between ^{205}Tl and ^{195}Pt, they also show coupling to a ^{13}C nucleus of one cyanide ligand (1:1 doublet) with a large coupling constant (12.7−7.2 kHz, cf. Table 1). By analogy with **II**, this $J(^{205}\mathrm{Tl}-^{13}\mathrm{C})$ can be assumed to arise from the interaction between thallium and the cyanide $\mathrm{C^A}$. Values of other coupling constants to the ^{13}C nuclei are significantly smaller (Table 1), and their variation for the compounds **III** and **IV**, in combination with the relatively broad signals (200−300 Hz), results in less well-resolved multiplets. Accurate $J(^{205}\mathrm{Tl}-^{13}\mathrm{C})$ values for all types of carbon nuclei could be obtained only for complexes **I** and **II**, and the number of coupled spins was determined directly from the ^{205}Tl NMR spectra. Below, we present the assignment of the ^{205}Tl and ^{13}C NMR spectra[28] for the species **I**, **III**, and **IV**; the latter two cases are supported by the results of spectral simulation.

Complex I. The ^{205}Tl NMR spectrum of **I** shows (similarly as for complex **II**) spin−spin coupling to ^{195}Pt, $\mathrm{C^A}$, and 1:4:6:4:1 pentets arising from coupling to four equivalent cyanides $\mathrm{C^C}$ (Figure 4a). This indicates that totally five cyanide ligands are present in the complex and the spin system can be described as $\mathrm{MX_4}$ for the carbon sites.

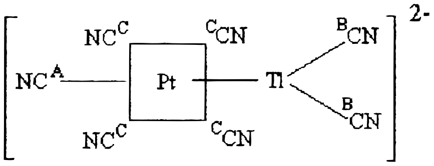
The ^{13}C NMR spectrum of this compound is fully compatible with the assignment and exhibits signals of two different groups of cyanide ligands positioned at 93.4 and 90.3 ppm with the intensity ratio 1:4, respectively. Both signals are split into doublets by spin−spin coupling to ^{205}Tl and are further split by ^{195}Pt. The chemical shift value and coupling constants of the more intensive signal are indicative of the $\mathrm{C^C}$ cyanides, which allows us to assign it to the four carbons of the $\mathrm{Pt(CN)_4}$ unit of **I**. The coupling constant of the remaining carbon to ^{205}Tl has the same value as that available from the ^{205}Tl NMR spectra (see above), confirming its assignment to the $\mathrm{C^A}$ cyanide, and leads to the following structure of this compound:

I



Complex III. Careful analysis of the multiplets appearing in the ^{205}Tl NMR spectrum (Figure 4c) showed that they result from spin−spin coupling between ^{205}Tl and two different ^{13}C sites with a similar magnitude of coupling constants, which leads to a deceptively simple spectrum. To establish the spin system and accurate values of the coupling constants, ^{205}Tl NMR spectra were simulated on the base of various models, followed by an iteration. This treatment led to the conclusion that only an $\mathrm{A_2MX_4}$ spin system (considering only the ^{13}C sites) fits to the experimental spectrum (Supporting Information). Therefore, it can be concluded that **III**, similarly to **II**, contains three groups of chemically equivalent cyanides and the only difference is that in **III** there is one more $\mathrm{C^B}$ cyanide bound to the thallium:

III



Fine structure of the ^{13}C NMR spectrum of **III** becomes observable only when the temperature of the solution is decreased to 273 K. Signals of three types of cyanide ligands can be detected at 156.9, 110.6 and 93.4 ppm with the intensity ratio 2:1:4, respectively, and are coupled to ^{205}Tl and ^{195}Pt (coupling to ^{203}Tl is also observed for the former two signals). These resonances can be unambiguously assigned to the $\mathrm{C^B}$, $\mathrm{C^A}$, and $\mathrm{C^C}$ cyanides, respectively (Table 1). In addition, the signal of $\mathrm{C^B}$ is split into a doublet with $J = 19$ Hz. By analogy with **II** we attribute it to the spin-spin coupling to the $\mathrm{C^A}$ nucleus (this coupling cannot be observed for the signal of $\mathrm{C^A}$ due to its relatively large linewidth, 53 Hz). The spin−spin coupling

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(26) Jameson, C. J. In *Multinuclear NMR*; Plenum Press: New York, 1987; pp 89−131.

(27) Green, M.; Howard, J. A. K.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1509−1514.

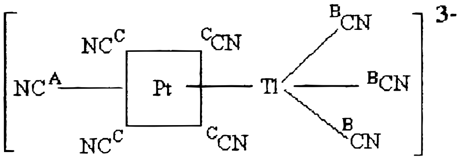
(28) The ^{195}Pt NMR spectra of the ^{13}C-enriched complexes **I**, **III**, and **IV** are fully in agreement with the structures proposed for these compounds on the basis of ^{205}Tl and ^{13}C NMR data. Because ^{195}Pt NMR spectra are less informative and do not provide any additional information, they are not discussed in this paper. A typical ^{195}Pt NMR spectrum is included in Supporting Information.

constants, $J(^{13}\mathrm{C}{-}^{205}\mathrm{Tl})$, obtained directly from ^{13}C NMR spectra of **III** (Table 1) are in good agreement with the values calculated from the ^{205}Tl spectra and, together with the chemical shift values and signal intensities, confirm the above structure of the complex.

Complex IV. The continuous decrease of the platinum−thallium coupling constant and the magnitudes of $J(^{205}\mathrm{Tl}{-}^{13}\mathrm{C})$ for the binuclear complexes **I** through **IV** (Table 1), in connection with cyanide ligand exchange, leads to only partially resolved signals with a pseudotriplet structure in the ^{205}Tl NMR spectra of **IV** (Figure 4d). In contrast to **III**, several possible spin systems can be found to fit the experimental spectrum; thus, additional information about the number of spins coupled to thallium is necessary.

Room temperature ^{13}C NMR spectra of the solutions containing **IV** as the main species show two relatively narrow peaks (line width ≈ 10 Hz) at 116.1 and 97.0 ppm with the intensity ratio 1:4, and coupled to ^{205}Tl and ^{195}Pt. These peaks were assigned to the $\mathrm{C^A}$ and $\mathrm{C^C}$ cyanides, respectively, of the binuclear complex (Table 1). In addition, a broad resonance (line width ≈ 330 Hz) centered at about 143 ppm is detected in the spectra. This signal is due to the fast exchange between the $\mathrm{C^B}$ cyanides of **IV** and those of $\mathrm{Tl(CN)_4^-}$ (30% of the total thallium in the solution, $\delta_{\mathrm{Tl(CN)_4^-}} = 145.0$ ppm). A decrease of the temperature in order to slow down the exchange process led to an increasing line width of the signal, and at 268 K it is broadened beyond detection; further cooling results in freezing of the sample. Other attempts to slow down the exchange and hence to resolve the signal by diluting the solution or by introducing an inert salt ($\mathrm{NaClO_4}$) to decrease the freezing point were not successful. Nevertheless, taking into account the concentrations of **IV** and $\mathrm{Tl(CN)_4^-}$ in solution (as obtained from ^{205}Tl NMR), the intensity of the signal $\mathrm{C^B}$ can be calculated, leading to the integral ratio of the three cyanide sites in the compound equal to 1:3:4. Therefore, we propose the following structure of **IV**:

IV



Simulation, and the following iteration of the ^{205}Tl NMR spectra of **IV** in terms of $\mathrm{A_3MX_4}$ spin system (for the carbon sites only) resulted in a calculated spectrum which is in good agreement with the experimental one (Supporting Information) and gave the values of the coupling constants between thallium and carbon: $J(^{205}\mathrm{Tl}{-}^{13}\mathrm{C^B}) = 52$ Hz and $J(^{205}\mathrm{Tl}{-}^{13}\mathrm{C^C}) = 256$ Hz; the latter coincides with the experimental value obtained from ^{13}C NMR (Table 1).

Trinuclear Pt−Tl−Pt Complex. The determination of the structure of the trinuclear Pt−Tl−Pt complex in solution was carried out in two steps. First, a selectively ^{13}C-labeled complex was prepared by the reaction between $\mathrm{Pt(^{12}CN)_4^{2-}}$ and $\mathrm{Tl(^{13}CN)_2^+}$ species. The ^{205}Tl NMR spectrum of the complex showed, in addition to coupling to ^{195}Pt giving a five-line spectrum (natural ^{13}C abundance, Figure 3), splitting of each signal into a 1:2:1 triplet (^{13}C-enriched complex, cf. Supporting Information). This is due to coupling to ^{13}C (cf. Supporting Information) which indicates presence of two equivalent cyanide ligands in the structure. The magnitude of this coupling constant (4600 Hz) is of the same order of magnitude as the values of $J_{\mathrm{Tl-C^A}}$ of the binuclear Pt−Tl compounds, and we assign it to $^{\mathrm{A}}$CN ligand occupying a trans position to thallium in the structure.

When both starting complexes, $\mathrm{Pt(CN)_4^{2-}}$ and $\mathrm{Tl(CN)_2^+}$, were enriched to 99% in ^{13}C, the ^{205}Tl NMR signals were additionally split into nine lines (cf. Supporting Information) due to coupling to the carbon nuclei of two equivalent $\mathrm{Pt(^CCN)_4}$ units. These findings are also confirmed by the ^{13}C NMR spectrum of the complex exhibiting (in the same way as for **I**) signals of only two groups of carbon nuclei with the intensity ratio 1:4 and chemical shifts compatible with assignment to $^{\mathrm{A}}$CN and $^{\mathrm{C}}$CN ligands, respectively. All NMR parameters for the trinuclear complex are given in Table 1. By combining all available data, the following structure of the trimer can be proposed:

V

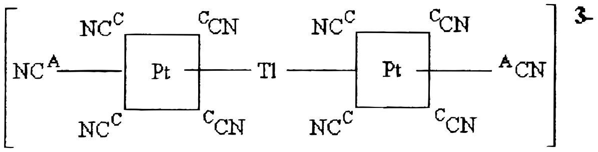


Table 2. Characteristic Raman Vibrational Frequencies ($\mathrm{cm^{-1}}$) of Binuclear Pt−Tl and Some Related Cyanide Compounds and Symmetric Stretching Force Constants ($\mathrm{N\ cm^{-1}}$) for the Metal−Metal Bond

complex	$^{\mathrm{A}}$CN	Tl(CN) ($^{\mathrm{B}}$CN)	$\mathrm{Pt(CN)_4}$ ($^{\mathrm{C}}$CN)	Pt−Tl	*K* (Pt−Tl)[a]
I	*b*	−	2200 s[c]	160 s, br	
II	2210 w, sh	2175 m, br	2199 s 2188 m, sh	161 s	1.53
III	2210 m	2162 s, br	2191 s 2179 m	157 s	
IV	2210 w	2161 s, br	2191 s 2179 m	157 s	1.45
$\mathrm{Tl^{III}(CN)^{2+}}$[d]		2200			
$\mathrm{Tl^{III}(CN)_3}$		2187			
$\mathrm{Pt^{II}(CN)_4^{2-}}$			2167 s 2148 m		
$\mathrm{Pt^{IV}(CN)_6^{2-}}$			2210 s 2202 m, sh		

[a] Only metal atom skeletons were used for calculations.[29] [b] No separate line was observed, probably due to overlap by a very strong band at 2200 $\mathrm{cm^{-1}}$. [c] The B_1 vibration frequency cannot be determined accurately due to overlapping bands from other complexes. [d] Frequency from ref 34.

B. Characterization of Binuclear Pt−Tl Cyano Complexes in Aqueous Solution by Raman Spectroscopy. Due to specific equilibria between the Pt−Tl species in solution only **II** and **IV** can be prepared as dominating bimetallic complexes, even if **IV** is in equilibrium with $\mathrm{Tl(CN)_4^-}$ and $\mathrm{Pt(CN)_4^{2-}}$.[20] This makes Raman spectra of the solutions containing **I**, **III**, and **V** difficult to interpret. Nevertheless, the Raman data of the bimetallic Pt−Tl complexes give important information, especially concerning the metal−metal bond. In the discussion below we deal mainly with the data on **II** and **IV**.

A typical feature of Raman spectra of all solutions containing the Pt−Tl compounds is the presence of a strong and sharp band in the low-frequency region, for compounds **II** and **IV** at 161 and 157 $\mathrm{cm^{-1}}$, respectively (Table 2), which is characteristic for a metal−metal (M−M) bond stretching.[29] The depolarization ratio, *r*, of these Raman bands, 0.23 and 0.26, respectively, is consistent with an assignment to a M−M′ stretching vibration. Generally, bimetallic compounds with single metal−metal bonds

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(29) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986; p 536.

unsupported by bridging ligands display M−M stretching bands at wavenumbers lower than 200 cm^{-1}, while multiple bonding or ligand bridging in conjunction with an M−M single bond leads to higher wavenumbers.[30] Our estimated values of the stretching force constants (Table 2) are characteristic for single bonds.[30,31]

The C≡N stretching region of the binuclear species is also informative and can provide additional support for the above structural considerations based on multinuclear NMR data. Spectra of **II** and **IV** show both four intense bands of coordinated cyanide. Comparison of these two spectra, together with the information on the mononuclear platinum and thallium cyanide complexes (Table 2), allows us to distinguish vibrations of three different types of cyanide ligands.

We assign the broad band at the lowest frequency, 2161−2175 cm^{-1}, with the intensity increasing from **II** to **IV**, and almost the same line width as for the $Tl(CN)_n^{3-n}$ species, to the ^{B}CN ligands bound to the thallium atom (Table 2). The two sharp bands, between 2179 and 2200 cm^{-1}, in the middle of each set of four bands from the compounds **II**−**IV** can be attributed to the symmetric (A_{1g}) and antisymmetric (B_{1g}) stretching vibrations of four equivalent cyanides (^{C}CN) of the $Pt(CN)_4$ unit in D_{4h} symmetry.[32]

The highest frequency band at 2210 cm^{-1} for all compounds **I**−**IV** is assigned to the ^{A}CN ligand (Table 2). Above, when discussing the NMR data, we have considered alternative positions of this cyanide ion in the structures of the binuclear Pt−Tl compounds. The vibration frequency indicates a terminal position of the ^{A}CN cyanide in the compounds, rather than a bridging one. It was found for a number of the cyano complexes of metals containing both terminal and bridging cyanides that ν(C≡N) vibrational transitions indicative of two types of cyanide ligands are detected separately with the bridging ones appearing at considerably lower frequencies. Thus the binuclear complex anion $[Re_2(CN)_6(dppm)_2]^{2-}$ containing a single Re−Re bond exhibits cyanide bands at 2097 and 2081 cm^{-1} for the terminal and at 1935 cm^{-1} for the bridging ligands.[24] A similar difference, about 100 cm^{-1}, between the terminal and bridging cyanide vibration frequencies was also observed for the binuclear vanadium compound $[V(CO)_4(CN)_2]_2^{4-}$.[33] No stretching vibrations of the cyanide ligand were detected below 2161 cm^{-1} for the series of binuclear Pt−Tl complexes **I**−**IV**, which strongly indicates that no bridging cyanide ligands are present. Moreover, the highest frequency, 2210 cm^{-1}, of the cyanide ligands in these complexes is consistent with strong s donation from the carbon centered HOMO resulting in strengthening of the C≡N bond.[23]

Such a structural arrangement is also consistent with the constant frequency of the ^{A}CN cyanide stretching vibration in the series of compounds **I-IV**, which indicates that the Pt−^{A}CN bond strength is almost not affected by the change of the number of cyanide ligands bound to thallium, and therefore the influence of cyanides $(^{B}CN)_n$ on the ^{A}CN group is not important.

Discussion

Structure of the Pt−Tl Species. Summarizing the results described in the previous section, four closely related binuclear compounds with a general formula $[(CN)_5Pt{-}Tl(CN)_{n-1}]^{(n-1)-}$ ($n = 1-4$), and a trinuclear complex $[(NC)_5Pt{-}Tl{-}Pt(CN)_5]^{3-}$ can be obtained in aqueous solution. The coordination environment of the platinum atom in the bimetallic Pt−Tl species consists of four equivalent cyanide ions forming a square plane around the metal, while the apical positions of the pseudo-octahedron are occupied by one cyanide ligand and the thallium atom. Information available from NMR measurements is not sufficient to clarify the structural arrangement of the cyanide ligands *bound to thallium* in the family of binuclear compounds and only general considerations based on comparison with related species could be presented. Recently, thallium(III) cyanide complexes in aqueous solution were thoroughly studied by using a combination of experimental methods, including X-ray techniques (LAXS, EXAFS).[34] It was shown that the $Tl(CN)_2^+$ complex has a linear structure with four weakly coordinated water molecules in equatorial positions. It seems reasonable that the linearity is preserved also when a cyanide ligand is replaced by a $Pt(CN)_5$ group, as in **II**. In contrast to complex **II**, this linear geometry is not present in **III** and **IV** as can be inferred from the observed equivalence of two and three ^{B}CN ligands, respectively. When the $Tl(CN)_3$ complex in aqueous solution is formed from $Tl(CN)_2^+$, the coordination number of thallium changes from 6 to 4; a pseudotetrahedral structure for $Tl(CN)_3(H_2O)$ was assumed.[34] A similar pyramidal arrangement of cyanide ligands around thallium may be present in the structure of $[(NC)_5Pt{-}Tl(CN)_3]^{3-}$ with the platinum atom of the $Pt(CN)_5$ unit completing the pseudotetrahedral structure. For the other $[(CN)_5Pt{-}Tl(CN)_{n-1}]^{(n-1)-}$ complexes in solution ($n = 1-3$), the remaining coordination sites of the thallium atom are probably occupied by water molecules.

The ^{205}Tl NMR chemical shift of the $[(NC)_5Pt{-}Tl{-}Pt(CN)_5]^{3-}$ complex is very close to that of **II**. The magnitudes of both J_{Tl-Pt} and J_{Tl-C^A} are only about half as large as those for **II**. This can be interpreted as a result of substitution of ^{B}CN ligand in **II** by a $Pt(CN)_5$ unit to form a linear NC−Pt−Tl−Pt−CN axis. In the structure of the Pt−Tl−Pt trimer the thallium atom can be considered as bridging between the two platinum moieties. Very recently the complex anion $[Tl\{Pt(C_6F_5)_4\}_2]^{2-}$ containing a linear Pt−Tl−Pt core with all metal atoms in oxidation state +2 has been prepared and structurally characterized.[7] The linear trinuclear M−Tl−M fragment was also found to be present in the complex anion $[Tl\{Cr(CO)_5\}_2]^-$ which contains, according to the authors,[35] Tl^{1-} as a four-electron building block. On the other hand, when thallium is in the oxidation state +1, the M-Tl-M structure is strongly bent due to a stereoactive electron lone pair at the central Tl^{I}; this was observed for complexes with M = Pt [6] and Ir.[36] Formation of a diamagnetic compound $[(NC)_5Co{-}Tl{-}Co(CN)_5]^{5-}$ (closely related to **V)** obtained from the reaction of thallium(I) with pentacyanocobaltate(II) ions in aqueous solution is also discussed in ref 37.

For platinum, this type of Pt−M−Pt coordination geometry seems to be relatively common. Trinuclear complexes with linear Pt−M−Pt entities have previously been reported for M

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[30] Shriver, D. F.; Cooper, C. B. In *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Heyden: London, 1980; Vol. 6, pp 127−157.

[31] Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Clarendon Press: Oxford, 1993; p 787 and references therein.

[32] Memering, M. N.; Jones, L. H.; Bailar, J. C. *Inorg. Chem.* **1973**, *12*, 2793.

[33] Render, D. *J. Organomet. Chem.* **1972**, *37*, 303−312.

[34] Blixt, J.; Glaser, J.; Mink, J.; Persson, I.; Persson, P.; Sandström, M. *J. Am. Chem. Soc.* **1995**, *117*, 5089−5104.

[35] Schiemenz, B.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1772−1774.

[36] Balch, A. L.; Nagle, J. K.; Olmstead, M. M.; Reedy, P. E. *J. Am. Chem. Soc.* **1987**, *109*, 4123−4124.

[37] Crouch, E. C. C.; Pratt, J. M. *J. Chem. Soc., Chem. Commun* **1969**, 1243.

= Pb(II),[38] Cu(II),[39] and Ag(I).[40] In all these compounds the platinum atom has the oxidation state +2 and the coordination number five in a square-pyramidal geometry, in contrast to the six-coordination found in the Pt−Tl−Pt complex prepared in this work.

Metal−Metal Bonding in the Pt−Tl Species. The most striking feature of the studied bimetallic complexes is certainly the direct Pt−Tl metal−metal bond which is convincingly detected by both the spin−spin coupling constant between ^{195}Pt and ^{205}Tl nuclei and the stretching frequency ν(Pt−Tl).

There are seven known compounds containing a direct Pt−Tl linkage.[1,5−10] Vibrational data for the metal−metal bond in these complexes are lacking, while values of $^1J(^{195}\mathrm{Pt}{-}^{205}\mathrm{Tl})$ were obtained for two of them, namely $[\mathrm{Tl(crown\text{-}P_2)Pt(CN)_2}]^+$ (3825 Hz)[5] and $[\mathrm{TlPt_3(CO)_3(PCy_3)_3}]^+$ (2032 Hz)[8] both with monovalent thallium. As can be seen from Table 1, the platinum−thallium coupling constants of the oligonuclear complexes **I-V** surpass the previously known values by an order of magnitude.

When spin−spin coupling constants involving such heavy elements as platinum and thallium are considered, relativistic effects have to be taken into account.[26] This is especially important for thallium due to the presence of s valence orbitals. The relativistic contraction of the 6s shell of thallium leads to an increase of 6s electron density on the nucleus. This in turn contributes to the dominant Fermi contact term (defined as being due to 6s orbitals) for spin−spin coupling[41] and is reflected in the large values of $J(^{205}\mathrm{Tl}{-}\mathrm{X})$ even for coupling with lighter atoms (X = ^{1}H, ^{13}C, and ^{31}P[42,43]). Thus, for instance, $^1J(^{205}\mathrm{Tl}{-}^{13}\mathrm{C})$ is 14 636 Hz in the $\mathrm{Tl^{III}(CN)^{2+}}$ cation.[14]

In this light, the dramatic difference in the $^1J(^{195}\mathrm{Pt}{-}^{205}\mathrm{Tl})$ values between the series of species **I-V** and the other Pt−Tl compounds may reflect varying proportions of thallium 6s character in the metal−metal bond caused by the oxidation state of the thallium atom. This phenomenon can be qualitatively considered in terms of the *n*s^2 "inert pair" effect which is a classical feature some p-block elements of the periodic table.[44,45] When in the monovalent oxidation state, the thallium atom essentially preserves its 6s^2 filled shell. The minimal participation of thallium(I) s electrons in bond formation is supposedly reflected by the very limited $\mathrm{Tl^I{-}X}$ spin−spin coupling. Indeed, although numerous compounds of $\mathrm{Tl^I}$ have been investigated using the ^{205}Tl NMR technique, only a few spin−spin coupling constants have been reported[42] and even the largest of them are substantially smaller than those for $\mathrm{Tl^{III}}$. An analogous, but not so strong lone pair effect has been observed for several complexes of main group elements and is usually associated with a negative contribution to the one-bond coupling constant. The removal of the lone pair results in large amplification of the coupling.[26]

In contrast to thallium which exhibits only a few examples of spin−spin coupling to another metal nuclei, numerous couplings between platinum and different metal nuclei can be found in the literature. A collection of the values of $^1J(^{195}\mathrm{Pt}{-}\mathrm{M})$ displays a remarkably wide range with little relationship to the metal oxidation state and the structure of the complex.[46]

The magnitude of the $^{195}\mathrm{Pt}{-}^{205}\mathrm{Tl}$ coupling constant found for the bimetalic complex **I** is not only the largest known between these nuclei, but also the largest hitherto reported between two different nuclei. The only larger coupling constant is that found for the homopolyatomic cation $\mathrm{Hg_3}^{2+}$ with a covalent Hg−Hg bond.[47] Similarly as for the platinum−thallium species, the enormous isotropic coupling constant, $^1J(^{199}\mathrm{Hg}{-}^{199}\mathrm{Hg})$ = 139 600 Hz, is due to the high 6s contribution to the Hg−Hg bond and the high 6s electron density at the mercury nucleus caused by the relativistic effects on this heavy atom.

Therefore, the large values of $J(^{195}\mathrm{Pt}{-}^{205}\mathrm{Tl})$ observed for the compounds **I−V** allow to exclude presence of monovalent thallium in the series of binuclear species. At the same time, in contrast to the recently prepared paramagnetic complex $[\mathrm{Tl\{Pt(C_6F_5)_4\}_2}]^{2+}$ containing $\mathrm{Tl^{II}}$,[7] the narrow NMR signals of the bimetallic species obtained in this work exclude the presence of unpaired electrons in the Pt−Tl complexes in solution. Despite the difference in magnetic properties of complexes, the donor−acceptor model proposed by Uson for the Pt−Tl bonding situation[7] seems to be appropriate also in the present case. Thus, for the complexes **I−V** the metal−metal interactions can be qualitatively interpreted as a donation of a pair of electrons from the $\mathrm{Pt^{II}}$ atom to the s valence orbital of $\mathrm{Tl^{III}}$. An analogous dative bond formalism was used earlier for an isoelectronic $\mathrm{Pt^{II}(d^8)} \rightarrow \mathrm{Hg^{II}(d^{10})}$ system.[48]

Previous theoretical studies of $\mathrm{Pt^{II}(CN)_4}^{2-}$ anion, which is closely related to the bimetallic Pt−Tl species **I−V** (all containing $\mathrm{Pt(CN)_4}$ units), showed 91% contribution of atomic platinum orbitals (mainly $5\mathrm{d}_{z^2}$) to the highest occupied molecular orbital.[2] The formation of a σ bond with contributions from the 6s orbital of thallium and the filled $5\mathrm{d}_{z^2}$ orbitals in planar d^8 complexes[1] is symmetry-allowed and gives rise to a strong covalent Pt−Tl bond in the family of bimetalic complexes.

We have already noted that a strong dependence of all NMR parameters on the number of cyanide ligands bound to the thallium atom is a characteristic feature of the Pt−Tl compounds **I−IV**. Table 1 shows a clear tendency of decreasing $^1J(^{195}\mathrm{Pt}{-}^{205}\mathrm{Tl})$ with increasing number of CN$^-$ in the binuclear species. Thus, when going from **I** to **IV**, an almost 50% decrease of the Pt−Tl coupling constant takes place. Taking into account the general trend of spin−spin coupling constants to decrease with increasing interatomic distance between the two bound atoms, it would be natural to attribute such a strong effect to a significant weakening of the bond between the two metal atoms. Nevertheless, when dealing with metal−metal bonds, especially between heavy atoms, the situation is not so clear. The lack of correlation between $^1J_{\mathrm{Pt-Pt}}$ and such indicators of Pt−Pt bond strength as ν(Pt−Pt) and interatomic distance has been discussed for several compounds.[49,50] Also, no relation was observed between the metal−metal separations and the

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corresponding spin−spin coupling constants in trichlorostannate complexes of platinum(II) containing a direct Pt−Sn bond.[51] This observation was referred to a very high sensitivity of the spin−spin coupling to electronic changes in the metal−metal bonding which does not significantly affect other properties of the bond.[52] Hence, taking into account the governing role of the 6s orbitals of thallium in the Pt−Tl coupling, marked changes in the values of $^{1}J_{\mathrm{Pt-Tl}}$ in complexes **I−IV** may arise from variation of the s character in metal−metal bonding resulting from coordination of extra CN^{-} ligands to the thallium atom.

To assess the Pt−Tl bonding situation in the family of binuclear species Raman stretching vibration of the metal−metal bond was helpful. In contrast to the values of $^{1}J(^{195}\mathrm{Pt}-^{205}\mathrm{Tl})$ obtained from NMR, which decrease by 35% when going from **II** to **IV**, the vibrational transition frequency of the Pt−Tl bond changes by only 4 cm^{-1} (Table 2). The corresponding decrease of the force constants is quite small (5%), which means that the metal−metal bond strength is only very slightly affected by the number of cyanides bound to the thallium atom. Taking into account both the large masses of the coupled metal atoms and the known weakening of the Tl−C bond in $Tl(CN)_n^{3-n}$ species upon increasing n,[34] it is reasonable that the overall strength of the Pt−Tl bond is only slightly sensitive to coordination of additional cyanide ligands to the thallium atom of the bimetallic compounds.[19]

Oxidation State of the Metals in the Binuclear Pt−Tl Complexes. The chemical shifts of ^{205}Tl NMR are usually very indicative of the oxidation state of thallium. Thus, in aqueous solution the range of chemical shifts for Tl^{III} is usually between +1800 and +3600 ppm (excluding a few heavy halide compounds) and for Tl^{I} between −200 and +200 ppm.[42,45] ^{205}Tl NMR chemical shifts for the species **I−IV** lie in the wide range between the values characteristic for Tl^{I} and cyanide complexes of Tl^{III} (Table 1 and ref 14). The lowest δ_{Tl} found for **I** is 786 ppm which is much closer to the range of monovalent than to trivalent thallium. Coordination of additional CN^{-} ligands to the thallium atom results in the same trend as for the $Tl(CN)_n^{3-n}$ complexes, namely an increase of the chemical shift (Table 1); for complex **IV** the shift is close to the range of $Tl^{III}(CN)_n^{3-n}$ species (2300−3000 ppm).

Similarly as for thallium, the values of ^{195}Pt NMR chemical shifts for the **I−IV** complexes lie between the two oxidation states of platinum in its cyano complexes, Pt^{IV} ($Pt(CN)_6^{2-}$) and Pt^{II} ($Pt(CN)_4^{2-}$), but with the opposite trend of the δ_{Pt} change with increasing n in $[(NC)_5Pt-Tl(CN)_{n-1}]^{(n-1)-}$ species (Table 1). δ_{Pt} is largest for **I**, only 180 ppm from the corresponding value for hexacyanoplatinate(IV), whereas δ_{Pt} for **IV** is only 280 ppm from tetracyanoplatinate(II). Therefore, in the studied binuclear complexes the decreasing shielding of the thallium nucleus when coordinating additional cyanide ligands is accompanied by an increasing shielding of the platinum nucleus. This is in good agreement with the donor−acceptor model of the Pt−Tl bond considered above. In the absence of a direct Tl−CN bond (as in **I**), the electron pair donated by platinum is largely localized on the valence orbitals of thallium and, accordingly, gives the highest s contribution to the Pt−Tl bond (for the series of the binuclear compounds) and the strongest coupling constant $^{1}J(^{195}\mathrm{Pt}-^{205}\mathrm{Tl})$. Coordination of the cyanide ions to thallium results in a smooth transfer of electron density from thallium back to platinum, decreasing the s-character of the metal−metal bond, which is in turn reflected by a decrease in the Pt−Tl spin−spin coupling and the opposite trends of the δ_{Pt} and δ_{Tl} values. Discrete oxidation states cannot be assigned to the metal atoms in these complexes, which can be considered to contain partially oxidized (between 2+ and 4+) platinum[53] and partially reduced (between 3+ and 1+) thallium.

A number of compounds comprising intermediate oxidation states of the metal in the range +2.25 to +2.40 have been found for platinum.[54] Complexes of platinum(III) are less common compared to Pt^{II} and Pt^{IV} but have been intensively studied during the past decade.[55] The vast majority of Pt^{III} compounds are binuclear and contain a Pt−Pt entity.[31] No partially reduced compounds have been reported for thallium. The only intermediate which can be considered between the two main oxidation states of thallium is the thermodynamically unstable Tl^{II}. Until now only three solid compounds of thallium(II) have been reported. Apart from the paramagnetic cation $[Tl\{Pt(C_6F_5)_4\}_2]^{2+}$ discussed above,[7] two other compounds, both containing a direct $Tl^{II}-Tl^{II}$ bond, have been prepared: the diamagnetic $[(Me_3Si)_3Si]_2Tl-Tl[Si(SiMe_3)_3]_2$[56] and the cluster $Tl_{0.8}Sn_{0.6}Mo_7O_{11}$[57] with unknown magnetic properties.

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 heteronuclear 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 $[(NC)_5Pt-Tl-Pt(CN)_5]^{3-}$ (**V**) can be obtained. Multinuclear NMR, supported by Raman spectroscopy, allows us to establish the stability of the metal−metal bond in aqueous solution and to distinguish three types of cyanide ligands in the complexes. Four equivalent cyanide ions form a square plane around the platinum atom, and one cyanide occupies an apical position trans to the thallium atom in the pseudo-octahedrally coordinated platinum. The number of cyanides bound to thallium varies from 0 to 3 in the binuclear species giving rise to four different complexes.

Data on nuclear spin−spin coupling constants and vibration frequencies are fully indicative of a direct and unsupported Pt−Tl bond in the oligonuclear complexes formed in solution. The estimated force constants for the Pt−Tl bonds are characteristic for single bonds. Taking into account the diamagnetic nature of the complexes in solution, the bonding situation in the Pt−Tl systems can be interpreted as a donation of two electrons which are shared by the two metals, where the thallium-related molecular metal−metal orbital accommodates electron density donated by platinum. Quantum mechanical calculations are clearly needed to clarify the details of the bonding situation between the two metals.

The strength of the metal−metal bonds as represented by the force constant is only slightly affected by change of the number of cyanide ligands in the binuclear complexes. On the other

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(53) This is also supported by the cyanide stretching vibrations of the $Pt(CN)_4$ unit in the family of the binuclear Pt−Tl compounds exhibiting $\nu(C\equiv N)$ values in the range between the frequencies of Pt^{II} and Pt^{IV} cyano complexes (Table 2).

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hand, the value of $^{1}J(^{195}\mathrm{Pt}-^{205}\mathrm{Tl})$ changes significantly with n in $[(\mathrm{CN})_5\mathrm{Pt}-\mathrm{Tl}(\mathrm{CN})_{n-1}]^{(n-1)-}$. Assuming that contact contribution dominates the spin−spin coupling mechanism, the large difference in the Pt−Tl coupling constants, varying between 71 and 38 kHz, may arise from different amount of thallium 6s character in the bond. This can be viewed as a shift of the electron density between the two metals due to the influence of additional cyanide ligands bonded to the thallium atom. Such an electron transfer is consistent with a smooth change of (i) shielding of the ^{195}Pt and ^{205}Tl nuclei, reflected by the values of their chemical shifts, which fall in the region between those for $\mathrm{Pt^{II}(CN)_4}^{2-}$ and $\mathrm{Pt^{IV}(CN)_6}^{2-}$, and $\mathrm{Tl^{III}(CN)}_n{}^{3-n}$ and $\mathrm{Tl^{I}}$, respectively, and (ii) C≡N stretching frequencies lying in the range between bi- and tetravalent platinum cyanides.

This shows that we deal with partially oxidized/reduced metal atoms. The most pronounced transfer of the electron pair between the two coupled metal centers takes place in the absence of cyanide ions coordinated to thallium; hence, the cyanide ligand stabilizes trivalent thallium and prevents its reduction by platinum(II).

Intermediate oxidation states are well-known for platinum, but for thallium this is the first report of formation in solution of a series of stable compounds containing diamagnetic thallium with oxidation state between +3 and +1. The dependence of the oxidation state of the metals on the number of the cyanide ligands coordinated to thallium in heterobinuclear complexes can be used for controlling the redox process between the two bound metals and the electronic properties of the intermediates formed can be studied with particular attention to their sensitivity to photoinduced electron-transfer reactions.

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Supporting Information Available: Output parameters from simulation of ^{205}Tl NMR spectra (spin−spin coupling constants, chemical shifts, line widths), figures showing experimental and simulated ^{205}Tl NMR spectra of aqueous solutions of **III** and **IV**, ^{205}Tl NMR spectra of partially and fully ^{13}CN-enriched complex **V**, Raman spectra (region of stretching vibrations of the CN group) of aqueous solutions of **II** and **IV**, and diagram showing ^{205}Tl and ^{195}Pt NMR chemical shifts of **I**−**IV** as a function of the number of cyano ligands bound to thallium (8 pages). Ordering information is given on any current masthead page.

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