

## Novel Pentacyano Complexes of Tri- and Tetravalent Platinum

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New pentacyano complexes of tri- and tetravalent platinum were obtained in aqueous solution and characterized by multinuclear NMR (<sup>195</sup>Pt, <sup>13</sup>C) supported by Raman spectroscopy. The complexes form as products of redox decomposition of metal–metal bonded platinum–thallium compounds. The trimetallic [(NC)<sub>5</sub>Pt–Tl–Pt(CN)<sub>5</sub>]<sup>3–</sup> yields a new dimeric compound of Pt(III), [(NC)<sub>5</sub>Pt–Pt(CN)<sub>5</sub>]<sup>4–</sup>. The latter is a rare representative of unbridged dimeric complexes of trivalent platinum; it was obtained through an oxidation of monomeric square-planar platinum(II) species by a metal complex. From the bimetallic compounds [(NC)<sub>5</sub>Pt–Tl(CN)<sub>n</sub>]<sup>n–</sup> (*n* = 0–2) tetravalent platinum complexes are formed. Depending on the Pt–Tl species, electron transfer is initiated either by heat or by exposition to light; it results in [Pt(CN)<sub>6</sub>]<sup>2–</sup> or in the hitherto unknown complexes [Pt(CN)<sub>5</sub>(OH)]<sup>2–</sup> and [Pt(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>–</sup>, with the <sup>195</sup>Pt NMR chemical shift values 1638.7 (±0.6) and 1766.7 (±0.6), respectively. Proton dissociation constant of [Pt(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>–</sup> has been determined, p*K*<sub>a</sub> = 2.51 (±0.01). In both Pt<sup>III</sup> and Pt<sup>IV</sup> pentacyano complexes platinum is hexacoordinated forming a pseudo-octahedron with two types of cyano ligands: four equivalent equatorial cyanides and one apical. Related platinum(IV) species, [Pt(CN)<sub>5</sub>X]<sup>2–</sup> (X = Cl, Br, I), have also been studied. In all the pentacyano complexes a pronounced trans influence is reflected in a substantial difference between the <sup>195</sup>Pt–<sup>13</sup>C spin–spin coupling constant for the apical (trans) and the equatorial (cis) carbon sites. In this respect, the studied X ligands can be ordered in a series of decreasing <sup>195</sup>Pt–<sup>13</sup>C<sub>trans</sub> coupling constant: H<sub>2</sub>O > Cl<sup>–</sup> > Br<sup>–</sup> > I<sup>–</sup> > OH<sup>–</sup> > CN<sup>–</sup>.

### Introduction

Platinum(II) cyano complexes are well-known, and numerous tetracyano and mixed cyano compounds with other ligands have been synthesized and characterized in solution and in solid.<sup>1</sup> However, corresponding compounds of platinum(IV) were obtained in the 1960s, but only a few crystal structures have been reported.<sup>2–6</sup> A series of solid salts, M<sub>2</sub>[Pt(CN)<sub>4</sub>X<sub>0.25–0.40</sub>] (M = balancing cation, X = Cl, Br), in which the average oxidation state of platinum is between II and III has also recently attracted a lot of interest.<sup>7</sup> In these structures, the planar Pt(CN)<sub>4</sub> units are stacked and the Pt–Pt distance is short (<3.0 Å) which gives rise to one-dimensional conductivity of the compounds.

Pentacyano complexes of tetravalent platinum are usually viewed as monosubstituted hexacyano species. To our knowledge, only three compounds of this type, [Pt<sup>IV</sup>(CN)<sub>5</sub>X]<sup>2–</sup>, have been reported (X = Cl, Br, I). Halopentacyano complexes can

be prepared by oxidative addition reaction of tetracyanoplatinum(II) with cyanogen iodide<sup>8–10</sup> or bromide<sup>11</sup> or by the action of Cl<sub>2</sub> or Br<sub>2</sub> on [Pt(CN)<sub>5</sub>I]<sup>2–</sup>.<sup>12</sup> Alternative pathways include substitution of hexachloroplatinum(IV) by cyanide<sup>13</sup> and reaction of dihalotetracyanoplatinum(IV) with cyanide.<sup>14</sup> The compounds have been subjected to spectroscopic studies in solution<sup>13,15,16</sup> and in the solid state,<sup>12,15</sup> revealing substantial halide dependent differences between *cis*- and *trans*-cyano ligands in pseudo-octahedral geometry of the platinum polyhedron. Surprisingly, no crystal structure data on [Pt(CN)<sub>5</sub>X]<sup>2–</sup> complexes have been reported.

The existence of homoligand pentacyano compounds [Pt(CN)<sub>5</sub>]<sup>n–</sup> has been a matter of discussion for at least one and a half centuries.<sup>17,18</sup> Several solids with the stoichiometry M<sub>2</sub>[Pt(CN)<sub>5</sub>]·H<sub>2</sub>O (where M is a balancing metal cation) have been

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prepared. These compounds were viewed either as mixed Pt<sup>II</sup>/Pt<sup>IV</sup> chains built of tetra- and hexacyano species of Pt(II) and Pt(IV), respectively, or as mononuclear complexes of Pt(III). Piccinin and Toussaint obtained crystals of K<sub>2</sub>Pt(CN)<sub>5</sub>·3H<sub>2</sub>O from nitric acid oxidation of platinum metal, presumably in the presence of cyanide ions.<sup>17</sup> From low-quality crystallographic data the authors found a relatively short Pt–Pt separation of 2.92 Å which excludes formation of the mixed valence chain structure.

Recently, we reported our structural<sup>19,20</sup> and equilibrium<sup>21</sup> studies of the family of oligometallic platinum–thallium cyano compounds containing (NC)<sub>5</sub>Pt- unit(s) directly bonded to the thallium atom. The complexes can be viewed as metastable intermediate products of the electron-transfer reaction between Pt(II) and Tl(III) leading to Pt(IV) and Tl(I). Depending on the bimetallic Pt–Tl cyano compound<sup>20</sup> and the experimental conditions, the redox reaction can yield a number of oxidized platinum cyano species and Tl(I). Here we report a study of hitherto unknown pentacyano complexes of tri- and tetravalent platinum in aqueous solution. These novel platinum compounds, which form as a result of redox decomposition of the oligonuclear Pt–Tl complexes, were characterized by multinuclear NMR, supported by Raman spectroscopy. For comparison, some related pentacyano species of platinum(IV) have also been considered.

## Experimental Section

**Warning!** Solutions containing cyanides should be treated with care due to a possible emission of poisonous gases: HCN in acidic medium, or (CN)<sub>2</sub> in oxidizing medium.

**Materials.** 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<sub>2</sub>Pt(CN)<sub>4</sub> with an excess of aqueous sodium perchlorate at 275 K and was used as a stock platinum solution. A concentrated (1.45 M) aqueous solution of Tl(ClO<sub>4</sub>)<sub>3</sub> in 3.77 M HClO<sub>4</sub> was obtained by anodic oxidation of TlClO<sub>4</sub>.<sup>22</sup> A concentrated acidic solution of Tl(NO<sub>3</sub>)<sub>3</sub> (1.42 M in 2.96 M HNO<sub>3</sub>) was prepared by direct dissolution of Tl<sub>2</sub>O<sub>3</sub> in nitric acid under heating. Solutions of thallium(III) cyanide complexes were synthesized as described previously.<sup>23</sup> The content of Tl<sup>I</sup> in the starting thallium solution varied from 1 to 3% of the total thallium concentration. For some NMR measurements <sup>13</sup>CN-enriched solutions (99%) were used; in this case, Tl<sup>III</sup>(<sup>13</sup>CN)<sub>n</sub><sup>3-n</sup> species were prepared using solid Na<sup>13</sup>CN, whereas Na<sub>2</sub>Pt(<sup>13</sup>CN)<sub>4</sub> salt was obtained from the exchange reaction between K<sub>2</sub>PtCl<sub>4</sub> and Na<sup>13</sup>CN in aqueous solution with molar ratio <sup>13</sup>CN/Pt = 6, followed by recrystallization of the tetracyanoplatinate salt. Anal. Calcd for Na<sub>2</sub>Pt(<sup>13</sup>CN)<sub>4</sub>·H<sub>2</sub>O: Pt, 53.1; Na, 12.5. Found: Pt, 54.4; Na, 12.6. Bimetallic Pt–Tl cyano complexes in aqueous solution were prepared by mixing solutions of Pt(CN)<sub>4</sub><sup>2-</sup> and Tl(CN)<sub>n</sub><sup>3-n</sup> (n = 2–4) at different Pt/Tl and cyanide-to-metal ratios as described previously.<sup>20,21</sup> The solid compound, [(NC)<sub>5</sub>PtTl], was precipitated from the solution containing the corresponding complex and 1.5 M perchloric or nitric acid.<sup>20</sup>

[Pt(<sup>13</sup>CN)<sub>5</sub>I]<sup>2-</sup>. The complex was prepared in aqueous solution according to the procedure<sup>8</sup> in which Pt(<sup>13</sup>CN)<sub>4</sub><sup>2-</sup> (0.1 mmol) was oxidized by the <sup>13</sup>C-enriched cyanogen iodide (0.12 mmol). The concentration of the resulting solution was 50 mM; the compound was not isolated.

[Pt(<sup>13</sup>CN)<sub>5</sub>Br]<sup>2-</sup>. The complex was obtained by in situ oxidation of the iodide in [Pt(<sup>13</sup>CN)<sub>5</sub>I]<sup>2-</sup> (0.1 mmol) by excess of bromine in aqueous solution.<sup>12</sup> The concentration of the resulting solution was 50 mM; the compound was not isolated.

[Pt(<sup>13</sup>CN)<sub>5</sub>Cl]<sup>2-</sup>. The complex was prepared by addition of an aqueous solution of <sup>13</sup>C-enriched sodium cyanide (0.78 mmol) to an aqueous solution of Na<sub>2</sub>PtCl<sub>6</sub> (0.13 mmol).<sup>13</sup> The concentration of the resulting solution was 50 mM; the compound was not isolated.

[Pt(CN)<sub>5</sub>H<sub>2</sub>O]<sup>-</sup> and [Pt(CN)<sub>5</sub>OH]<sup>2-</sup>. Both complexes were prepared in solution by continuous heating at 80 °C under stirring of a suspension of the solid compound [(NC)<sub>5</sub>PtTl] (0.09 mmol) in a slightly alkaline aqueous solution (1 mL, pH ≈ 8, adjusted by NaOH). Homogeneous, transparent and colorless solution was obtained within 12 h. The only thallium species detected in the solution by <sup>205</sup>Tl NMR was Tl<sup>I</sup>. pH of the resulting solutions was adjusted with 0.80 M HClO<sub>4</sub> (down to pH = 1.32) and 0.39 M NaOH (up to pH = 8.60) for the species [Pt(CN)<sub>5</sub>H<sub>2</sub>O]<sup>-</sup> and [Pt(CN)<sub>5</sub>OH]<sup>2-</sup>, respectively. Solutions of the fully <sup>13</sup>C-enriched complexes were prepared in the same way, but from [(N<sup>13</sup>C)<sub>5</sub>PtTl].

[(NC)<sub>2</sub>Pt–Pt(CN)<sub>5</sub>]<sup>4-</sup>. The species was obtained in solution by dropwise addition of 0.5 mL of a solution of Tl(CN)<sub>2</sub><sup>+</sup> (0.15 mmol Tl(ClO<sub>4</sub>)<sub>3</sub>, 0.3 mmol NaCN, pH 2 adjusted by NaOH) to 1 mL of a solution of Na<sub>2</sub>Pt(CN)<sub>4</sub> (0.9 mmol). The pH of the resulting colorless solution was adjusted with 1.3 M NaOH up to pH = 2.6. The compound was not isolated, and a few minutes after the addition of Tl(CN)<sub>2</sub><sup>+</sup> the only thallium species detected in the solution by <sup>205</sup>Tl NMR was Tl<sup>I</sup>. All attempts to prepare solid phase containing this compound were unsuccessful.

**Analysis.** pH values were measured by a combination electrode radiometer GK2104C connected to a Radelkis OP-208/1 pH meter. The electrode readings were calibrated to pH values using the method of Irving et al.<sup>24</sup> for pH > 1 and by direct calibration for pH < 1.

**NMR Measurements.** NMR spectra were recorded with Bruker AC200, AM400, and DRX500 spectrometers at a probe temperature of 298(±0.5) K. Typical NMR parameters were as follows:

<sup>205</sup>Tl NMR (AM400): spectrometer frequency (SF) = 230.8 MHz; spectral window (SW) = 100 kHz; pulse width (PW) = 14 μs (flip angle ~60°); pulse repetition time 0.58 s; digital resolution 12 Hz/point. The chemical shifts are referred in ppm toward higher frequency from the <sup>205</sup>Tl NMR signal of an aqueous solution of TlClO<sub>4</sub>, extrapolated to infinite dilution.

<sup>195</sup>Pt NMR: SF = 42.8 MHz (also 85.6 and 107.5); SW = 10–50 kHz; PW = 12 μs (flip angle ~60°); pulse repetition time 0.58 s; digital resolution 8 Hz/point. The chemical shifts were measured relative to an external standard of aqueous 0.1 M Na<sub>2</sub>PtCl<sub>6</sub> which is 4533 ppm to higher frequency from Ξ(<sup>195</sup>Pt) = 21.4 MHz at 25 °C.<sup>25,26</sup>

<sup>13</sup>C NMR: SF = 50.3 (100.6) MHz; SW = 20 kHz; PW = 7 μs (flip angle ~18°); pulse repetition time 1.39 s; digital resolution 1.2 Hz/point; NS = 1000–10000. The chemical shifts were measured in ppm toward higher frequency with respect to an external signal of a water-soluble sodium derivative of TMS.

**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 contained in glass cuvettes were recorded by means of Dilor Z24 triple monochromator at a spectral bandwidth of 4 cm<sup>-1</sup> using photon counting.

## Results and Discussion

[Pt<sup>III</sup>(CN)<sub>5</sub>]<sub>2</sub><sup>4-</sup> Species. The recently prepared bimetallic Pt–Tl complexes [(NC)<sub>5</sub>Pt–Tl(CN)<sub>n</sub>]<sup>n-</sup> (n = 0–3) (Figure 1) are usually very inert toward redox decomposition and can be kept

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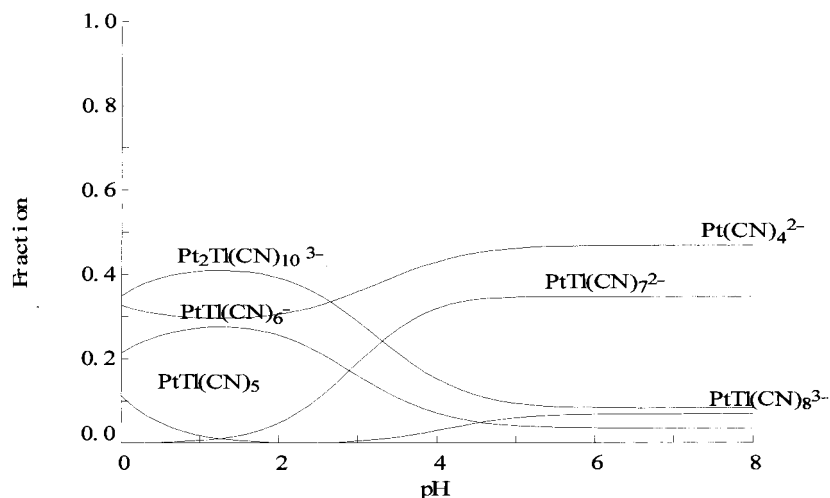
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**Figure 1.** Typical distribution of platinum-containing species in aqueous solution as a function of pH, calculated using the known stability constants.<sup>21</sup>  $[\text{Pt}]_{\text{tot}} = 100 \text{ mM}$ ,  $[\text{Tl}]_{\text{tot}} = 50 \text{ mM}$ ,  $[\text{CN}]_{\text{tot}} = 550 \text{ mM}$ . Redox decomposition of the bimetallic Pt–Tl complexes is not taken into account.

in solution for years in the dark at room temperature (295 K).<sup>20</sup> In contrast to this, in solutions containing significant amounts of the trinuclear species  $[(\text{NC})_5\text{Pt-Tl-Pt}(\text{CN})_5]^{3-}$ , preferably formed at high ratio of  $\text{Pt}(\text{CN})_4^{2-}/\text{Tl}(\text{CN})_2^+$ , a redox decomposition takes place and under certain conditions all thallium can be reduced to Tl(I). However, no  $[\text{Pt}(\text{CN})_6]^{2-}$  complex (expected to form as a result of the final oxidation of the platinum cyano compounds in the presence of excess of cyanide) was detected in  $^{195}\text{Pt}$  NMR spectra. The only  $^{195}\text{Pt}$  NMR resonance observed in these (natural abundance of  $^{13}\text{C}$ ) solutions—apart from the characteristic signals of the bimetallic Pt–Tl species and the signal of the  $\text{Pt}(\text{CN})_4^{2-}$ <sup>27</sup>—was an intensive singlet peak positioned at 116 ppm.

It was found that cyano ligands of the tetracyanoplatinate(II) are inert with respect to the ligand exchange with the thallium cyano complexes. This allowed preparation of the trinuclear species  $[(\text{NC})_5\text{Pt-Tl-Pt}(\text{CN})_5]^{3-}$  selectively labeled either in axial or in equatorial positions of the platinum pseudooctahedron by a reaction between  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{Tl}(\text{CN})_2^+$ , or  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{Tl}(\text{CN})_2^+$ , respectively.<sup>20</sup>

When the reaction was carried out between  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{Tl}(\text{CN})_2^+$  complexes, the signal at 116 ppm appeared as a symmetrical multiplet (Figure 2a). It has been demonstrated for several platinum complexes by Appleton et al.<sup>28–31</sup> that patterns of this type are not obtained through  $^{195}\text{Pt-X}$  coupling in a mononuclear complex. These patterns can be easily explained in terms of a binuclear symmetrical complex containing a Pt<sup>III</sup>–Pt<sup>III</sup> bond, with both Pt atoms coordinated by the same type of ligands. In such compounds, the  $^{195}\text{Pt}$  nuclei are chemically equivalent but are rendered magnetically nonequivalent by coupling to the X nuclei.<sup>32,33</sup> In this light the multiplet at 116 ppm can be assigned to the dimeric compound of trivalent platinum,  $[(\text{NC})_5\text{Pt-Pt}(\text{CN})_5]^{4-}$ . The two  $^{13}\text{C}$  atoms occupy

apical positions in each of the pentacyano units, and therefore the  $^{195}\text{Pt}$  spectrum (natural abundance of  $^{195}\text{Pt}$  is 33.7%) should appear as a probability-weighted superposition of two isotopomers with (i) one  $^{195}\text{Pt}$  nucleus (A part of the AXX' spectrum) and (ii) two  $^{195}\text{Pt}$  nuclei (AA' part of AA'XX' spectrum, one-half of the intensity of the AXX' spectrum).

The  $^{13}\text{C}$  spectrum for this complex consists of the central singlet at 93.3 ppm (from the isotopomer with no  $^{195}\text{Pt}$  nuclei) symmetrically flanked by peaks from isotopomers with one (X part of AXX' spectrum) and two (X part of AA'XX' spectrum)  $^{195}\text{Pt}$  nuclei with the intensity ratio 4:4:1, respectively (Figure 2b). Simulation of the spectra on the basis of these spin models, followed by an iteration, resulted in determination of the coupling constants  $^1J(\text{Pt-C})$ ,  $^2J(\text{Pt-C})$ ,  $^1J(\text{Pt-Pt})$ , and  $^3J(\text{C-C})$  ( $\text{C} = \text{C}_{\text{trans}} = \text{X}$ ) (Table 1 and Supporting Information, Figures S1–S3).

When the reaction was carried out between  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{Tl}(\text{CN})_2^+$ , the species  $[(\text{NC})_5\text{Pt-Pt}(\text{CN})_5]^{4-}$  was obtained with  $^{13}\text{C}$ -labeled equatorial sites of the platinum polyhedra. This allowed us to acquire information on the remaining coupling constants of the dimer. The final confirmation was obtained from the spectra of the fully  $^{13}\text{C}$  enriched Pt–Pt complex synthesized from platinum and thallium cyano species in which all cyanide was in form of  $^{13}\text{C}$  (Table 1 and Supporting Information).

The chemical shift of the  $[(\text{NC})_5\text{Pt-Pt}(\text{CN})_5]^{4-}$  species is close to the average of those for  $\text{Pt}^{\text{II}}(\text{CN})_4^{2-}$  and  $\text{Pt}^{\text{IV}}(\text{CN})_6^{2-}$  complexes (Table 1), which indicates the presence of trivalent platinum in the dimeric compound. Similarly, the specific “Pt<sup>III</sup> region” positioned between the corresponding mononuclear di- and tetravalent Pt species was considered for both the bridged binuclear platinum(III) complexes<sup>28–30</sup> and for an unsupported Pt<sup>III</sup> dimer,  $[\text{PtCl}(\text{acac})_2]_2$ .<sup>34</sup>

(27) However, in solutions containing excess  $[\text{Pt}(\text{CN})_4]^{2-}$ , the equilibrium between the complexes  $[(\text{NC})_5\text{Pt-Tl}(\text{CN})_n]^{3-n}$  ( $n = 0-3$ ) and  $[(\text{NC})_5\text{Pt-Tl-Pt}(\text{CN})_5]^{3-}$  (Figure 1) is shifted toward Pt–Tl–Pt; here, also the  $[\text{Pt}(\text{CN})_4]^{2-}$  signal is observed.

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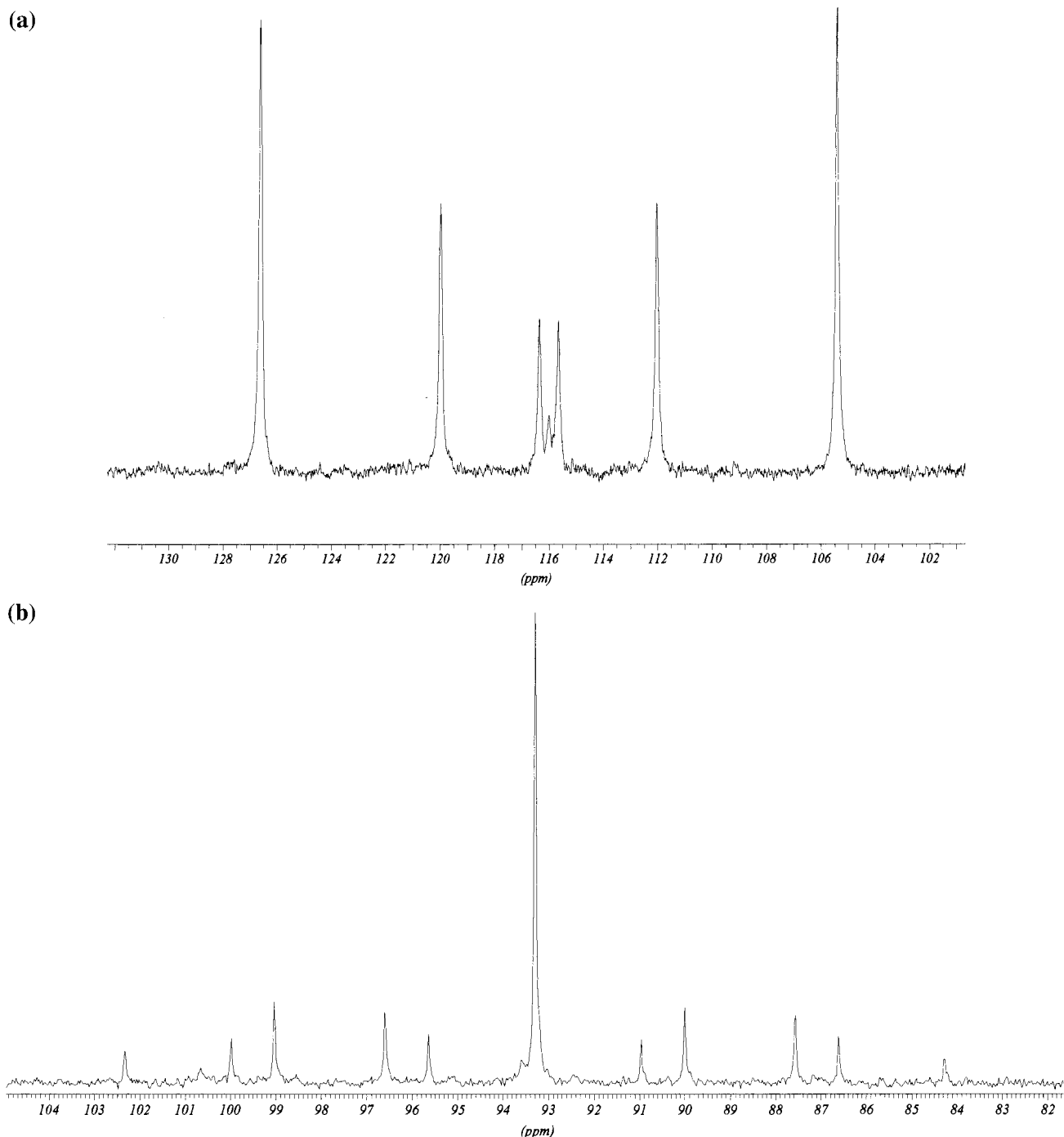
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(33) NMR spectra of the studied Pt–CN solution recorded at different magnetic fields (SF = 42.8 and 85.6 MHz) result in the same multiplet type confirming that it is not an exact superposition of separate multiplets at both chemical shifts.



**Figure 2.** NMR spectra of the complex  $[(\text{NC})_5\text{Pt}-\text{Pt}(\text{CN})_5]^{4-}$  formed in an aqueous solution containing starting species: 100 mM  $[\text{Pt}^{12}\text{CN}]_4^{2-}$ , 50 mM  $\text{Ti}^{3+}$ , and 100 mM  $\text{Na}^{13}\text{CN}$  at pH 0.43. (a)  $^{195}\text{Pt}$  NMR; (b)  $^{13}\text{C}$  NMR.

Most of the binuclear  $\text{Pt}^{\text{III}}-\text{Pt}^{\text{III}}$  compounds contain supporting ligands (carboxylato-, sulfato-, phosphato-, pyrophosphito-, etc. bridges) forming a “lantern structure”.<sup>35,36</sup> The one-bond Pt–Pt couplings in these complexes cover a wide range of values from 700 up to 6800 Hz and are significantly dependent on both axial and bridging ligands.<sup>28,30</sup> Few dimeric complexes of trivalent platinum with nonbuttressed metal–metal bond were found very recently,<sup>34,37–39</sup> and no information about spin–spin coupling constants between platinum nuclei in such compounds

is available. Nevertheless, the relatively large  $J(\text{Pt}-\text{Pt})$  value of  $\sim 1800$  Hz<sup>40</sup> found for the dimeric  $[(\text{NC})_5\text{Pt}-\text{Pt}(\text{CN})_5]^{4-}$  species is indicative of a direct metal–metal bond in the compound.

The bonding situation between the  $\text{Pt}^{\text{III}}$  atoms in the  $\text{Pt}_2^{6+}$  entity is usually considered on the basis of the  $\sigma^2\pi^4\delta^2\delta^*2\pi^*4$  orbital configuration giving rise to a single metal–metal

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(40) Due to superposition of at least two spin systems, overlapping peaks do not allow this value to be refined with better accuracy than 100 Hz.



**Table 1.** NMR Parameters for Pentacyano Compounds of Platinum and Some Related Complexes in Aqueous Solution

species	$\delta_{\text{Pt}}$ (ppm)	$\delta_{\text{cisC}}$ (ppm)	$\delta_{\text{transC}}$ (ppm)	$^1J_{\text{Pt-cisC}}$ (Hz)	$^1J_{\text{Pt-transC}}$ (Hz)	$^2J_{\text{transC-cisC}}$ (Hz)
[Pt(CN) <sub>4</sub> ] <sup>2-</sup>	-213	130.2		1031		
[Pt(CN) <sub>5</sub> H <sub>2</sub> O] <sup>-</sup>	1767	95.8	65.6	828	1096	4.9
[Pt(CN) <sub>5</sub> Cl] <sup>2-</sup> <sup>a</sup>	1234	95.8	78.8	824	1024	5.1
[Pt(CN) <sub>5</sub> Br] <sup>2-</sup> <sup>a</sup>	911	94.1	80.0	824	996	4.5
[Pt(CN) <sub>5</sub> I] <sup>2-</sup> <sup>a</sup>	319	91.2	77.7	828	921	4.4
[Pt(CN) <sub>5</sub> OH] <sup>2-</sup>	1639	98.4	83.2	846	904	4.7
[Pt(CN) <sub>5</sub> Tl] <sup>b</sup>	474	90.3	93.4	820	909	
[Pt(CN) <sub>5</sub> TlCN] <sup>-b</sup>	383	91.1	101.7	821	843	
[Pt(CN) <sub>5</sub> Tl(CN) <sub>2</sub> ] <sup>2-b</sup>	184	93.4	110.6	832	783	
[Pt(CN) <sub>5</sub> Tl(CN) <sub>3</sub> ] <sup>3-b</sup>	68	97.0	116.1	843	742	
[Pt(CN) <sub>5</sub> ] <sub>2</sub> Tl <sup>3-b</sup>	599	95.5	117.0	858	700	
[Pt(CN) <sub>5</sub> ] <sub>2</sub> <sup>4-c</sup>	116	100.6	93.2	878	618	5.2
[Pt(CN) <sub>6</sub> ] <sup>2-</sup>	653	88.8		806		

<sup>a</sup> Some of the parameters for the complexes [(NC)Pt(CN)<sub>4</sub>X]<sup>2-</sup> (X = Cl, I) have been reported previously in refs 13 and 16. <sup>b</sup> Data from ref 20. <sup>c</sup> Other coupling constants refined for this complex:  $^1J_{\text{Pt-Pt}} = 1800$  Hz (ref 40),  $^2J_{\text{Pt-cisC}} = 19.8$ ,  $^2J_{\text{Pt-transC}} = 291$ ,  $^3J_{\text{transC-transC}} = 48$  Hz. The analysis of the spectra also shows that  $^1J(\text{Pt-C}_{\text{cis}})$  and  $^2J(\text{Pt-C}_{\text{cis}})$  coupling constants have the opposite sign.

**Table 2.** Raman Data for Pentacyano Complexes of Platinum(IV) and for [Pt<sup>III</sup>(CN)<sub>5</sub>]<sub>2</sub><sup>4-</sup> in Aqueous Solution<sup>a</sup>

[Pt(CN) <sub>6</sub> ] <sup>2-</sup>	[Pt(CN) <sub>5</sub> Cl] <sup>2-b</sup>	[Pt(CN) <sub>5</sub> Br] <sup>2-b</sup>	[Pt(CN) <sub>5</sub> I] <sup>2-b</sup>	[Pt(CN) <sub>5</sub> H <sub>2</sub> O] <sup>-</sup>	[Pt(CN) <sub>5</sub> OH] <sup>2-</sup>	[Pt <sup>III</sup> (CN) <sub>5</sub> ] <sub>2</sub> <sup>4-</sup>
2211 vs (p) <sup>c</sup>	2204.9 (p)	2203.0 (p)	2199.5 (p)	2207 vs (p)	2202 vs (p)	2208 w (p)
2200 m (d)	2192.7 (d)	2195.5 (d)	2187.7 (d)	2196 m (d)	2190 m (d)	2192 vs (p)
			2179.5 (d)			2177 m (p)
				630 m (p)	546 m (p)	2161 s (p)
467 m (p)	462.9 (p)	465.8 (p)	467.0 (p)	464 s (p)	464 m (p)	504 w (p)
		452.5 (p)	432.9 (p)			467 s (p)
426 w (d)						400 m (p)
	329.5 (p)	226.0 (p)	180.6 (p)			145 s (p)
109 w (d)	109.1 (d)	105.2 (d)	107.4 (d)			

<sup>a</sup> Frequencies are expressed in cm<sup>-1</sup>. <sup>b</sup> From ref 15. <sup>c</sup> (p) polarized band; (d) depolarized band.

bond.<sup>35,36,41a</sup> Depending on the bridging and axial ligands, the Pt-Pt distances vary from 2.4 to 2.8 Å<sup>36</sup> while the values in the three nonbridged structures [Pt<sub>2</sub>Cl<sub>6</sub>{HN=C(OH)C(CH<sub>3</sub>)<sub>3</sub>}]<sub>4</sub>,<sup>37</sup> [Pt(C<sub>8</sub>doH)<sub>2</sub>Cl]<sub>2</sub>,<sup>38</sup> and [Pt(C<sub>12</sub>doH)<sub>2</sub>Cl]<sub>2</sub><sup>39</sup> are very similar: 2.694, 2.696, and 2.708 Å, respectively. A characteristic Raman absorption at 139 cm<sup>-1</sup> assigned to the Pt-Pt stretch was also reported for [Pt(C<sub>8</sub>doH)<sub>2</sub>Cl]<sub>2</sub>.<sup>38</sup> In the complex [PtCl(acac)<sub>2</sub>]<sub>2</sub>, the corresponding Raman band was observed at 144 cm<sup>-1</sup>.<sup>34</sup> A value of 145 cm<sup>-1</sup> for the symmetrical stretching frequency (Pt-Pt) obtained in this study from Raman spectra of the [(NC)<sub>5</sub>Pt-Pt(CN)<sub>5</sub>]<sup>4-</sup> complex in aqueous solution (cf. Table 2) serves as a strong support of the presence of a nonbuttressed Pt-Pt bond in the cyano dimer compound. The remaining Raman frequencies of [(NC)<sub>5</sub>Pt-Pt(CN)<sub>5</sub>]<sup>4-</sup> are also given in Table 2. By analogy with vibrational spectra of the platinum pentacyano complexes the bands at 467 and 400 cm<sup>-1</sup> can be assigned to A<sub>1</sub> stretching mode of the planar and apical Pt-C vibrations, respectively.

Similar bonding situation with pronounced character of the metal-metal bond in [(NC)<sub>5</sub>Pt-Pt(CN)<sub>5</sub>]<sup>4-</sup> is also indicated by the metal-ligand interactions. For the complex [Pt<sub>2</sub>Cl<sub>6</sub>{HN=C(OH)C(CH<sub>3</sub>)<sub>3</sub>}]<sub>4</sub> containing chloride atoms both in equatorial (*cis*) and axial (*trans*) positions of the platinum polyhedra, the much longer Pt-Cl<sub>ax</sub> distance is characteristic for a large *trans* influence exerted by the Pt<sup>III</sup>-Pt<sup>III</sup> bond.<sup>37</sup> Considering the lack of direct information on the Pt-C bond lengths in the pentacyano platinum(III) dimer, spin-spin coupling constants between the <sup>195</sup>Pt and <sup>13</sup>C nuclei can be used for estimation of the metal-ligand interactions (remembering that both the Pt-CN

bond strength and the amount of s-electron contribution will influence these constants). As can be seen in Table 1,  $^1J(\text{Pt-C}_{\text{trans}})$  is much smaller than  $^1J(\text{Pt-C}_{\text{cis}})$ , indicating strong *trans* influence for [(NC)<sub>5</sub>Pt-Pt(CN)<sub>5</sub>]<sup>4-</sup>.

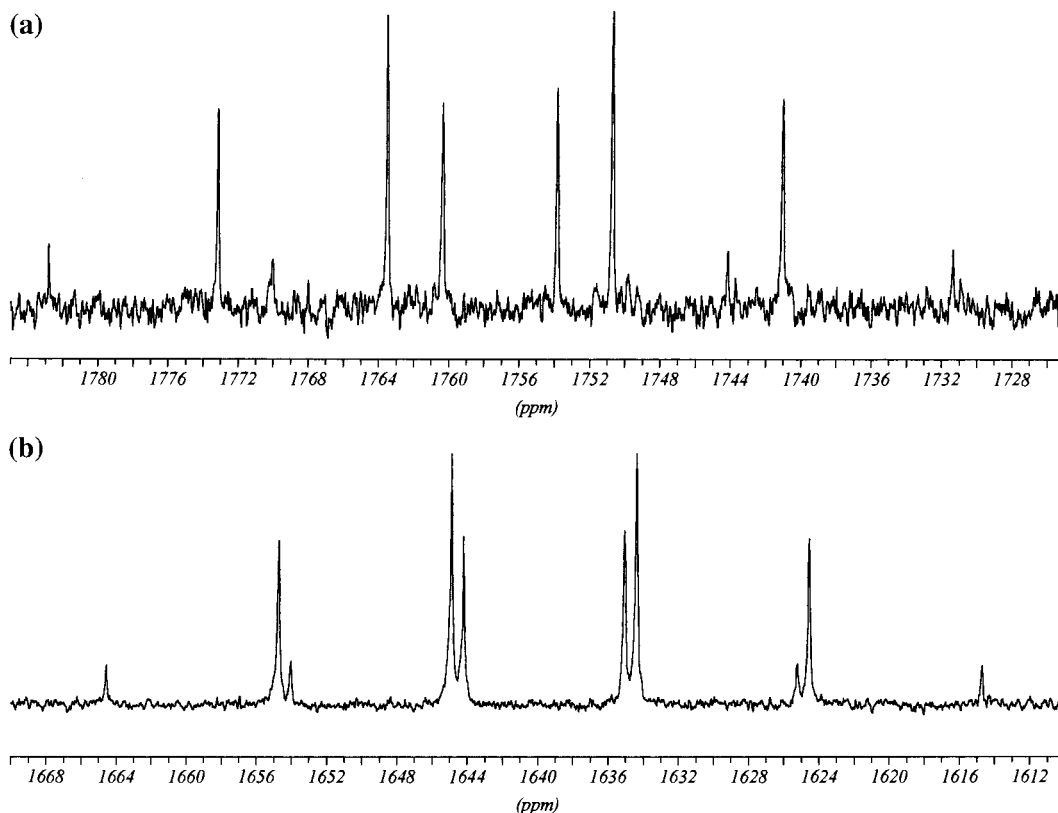
From the five possible isoelectronic d<sup>7</sup>d<sup>7</sup> systems, namely Co<sub>2</sub><sup>4+</sup>, Rh<sub>2</sub><sup>4+</sup>, Ir<sub>2</sub><sup>4+</sup>, Ni<sub>2</sub><sup>6+</sup>, and Pd<sub>2</sub><sup>6+</sup>, the bis-rhodium(II,II) compounds are best established and demonstrate a marked similarity in the bonding with the Pt<sub>2</sub><sup>6+</sup> analogues. As for platinum(III), among the large number of bridged Rh<sup>II</sup>-Rh<sup>II</sup> species only few unsupported compounds have been reported.<sup>36</sup> At the same time the information on cyano derivatives of divalent rhodium is lacking. It is quite interesting that the cyanides of divalent cobalt exhibit features very similar to those of the platinum(III) cyano complexes. In our recent paper<sup>20</sup> we have made a comparison between the trinuclear Pt-Tl-Pt cyano species and its cobalt(II) analogue [(NC)<sub>5</sub>Co-Tl-Co(CN)<sub>5</sub>]<sup>5-</sup>, obtained from the reaction of thallium(I) with [Co(CN)<sub>5</sub>]<sup>3-</sup>.<sup>41b</sup> Another example of the close similarity between platinum and cobalt cyano complexes can be the well-known Adamson's salt, [Co<sub>2</sub>(CN)<sub>10</sub>]<sup>6-</sup>. The crystal structure of this complex with barium as cation exhibits (apart from the short Co-Co distance of 2.80 Å) a square-pyramidal geometry of the cyanide ligands around the cobalt atom,<sup>42,43</sup> which closely resembles the proposed structure of the platinum(III) cyano dimer. Similarly as for the [(NC)<sub>5</sub>Pt-Pt(CN)<sub>5</sub>]<sup>4-</sup> species, the metal-metal bond in the binuclear cobalt(II) compound has a pronounced *trans* influence: Co-C<sub>ax</sub> is substantially longer than Co-C<sub>eq</sub>.

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**Figure 3.**  $^{195}\text{Pt}$  NMR spectra of 50 mM aqueous solutions of the fully  $^{13}\text{C}$ -enriched complexes  $[\text{Pt}(\text{CN})_5(\text{H}_2\text{O})]^-$  (a) and  $[\text{Pt}(\text{CN})_5(\text{OH})]^{2-}$  (b) obtained from decomposition of the solid compound  $[(\text{N}^{13}\text{C})_5\text{Pt-Tl}]$  at pH 1.12 and 5.46, respectively.

It is reasonable to assume that after the dissociation of the Pt–Tl bond an extra ligand will be coordinated by the platinum atom to fill the vacant sixth position of the Pt(IV) pseudo-octahedron.<sup>47</sup> In the studied aqueous platinum-cyano system only a water molecule can saturate the platinum coordination sphere in the pentacyano complex, as shown in Scheme 2.

Usually, the degree of protonation of the oxygen atoms has a profound effect on the platinum complexes through the Pt–O bond which is in turn reflected in the  $^{195}\text{Pt}$  NMR shift.<sup>28,48,49</sup> The pentacyano species exhibits a strong pH dependence of the platinum chemical shift. The two well-defined pH regions allow to discern the complexes  $[\text{Pt}(\text{CN})_5(\text{H}_2\text{O})]^-$  and  $[\text{Pt}(\text{CN})_5(\text{OH})]^{2-}$  (Figure S9 in Supporting Information and Table 1). Due to the fast exchange of the proton between the two species only a time-averaged  $^{195}\text{Pt}$  signal could be observed. The observed chemical shift of this peak is a direct function of the individual chemical shifts of  $[\text{Pt}(\text{CN})_5(\text{H}_2\text{O})]^-$  ( $\delta_{\text{H}_2\text{O}}$ ) and  $[\text{Pt}(\text{CN})_5(\text{OH})]^{2-}$  ( $\delta_{\text{OH}}$ ) and the molar fractions of these complexes ( $P_{\text{H}_2\text{O}}$  and  $P_{\text{OH}}$ ):

$$\delta_{\text{obs}} = \delta_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}} + \delta_{\text{OH}}P_{\text{OH}}$$

Substituting the equation into the expression for the protonation constant (based on concentrations), we obtain

$$\text{p}K_{\text{a}} = \text{pH} + \log[(\delta_{\text{OH}} - \delta_{\text{obs}})/(\delta_{\text{obs}} - \delta_{\text{H}_2\text{O}})]$$

(47) Formation of a square-pyramidal pentacyano polyhedron of platinum(IV) in aqueous solution seems improbable: low-spin  $d^6$  complexes prefer six-coordinate geometry.

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Experimental ( $\delta_{\text{obs}}$  vs pH) data were least-squares fitted giving the proton dissociation constant of  $[\text{Pt}(\text{CN})_5(\text{H}_2\text{O})]^-$  (50 mM in 1 M NaClO<sub>4</sub>),  $\text{p}K_{\text{a}} = 2.51 (\pm 0.01)$ , and the values of  $\delta_{\text{H}_2\text{O}}$  and  $\delta_{\text{OH}}$  of  $1766.7(\pm 0.6)$  and  $1638.7(\pm 0.6)$  ppm, respectively.<sup>50,51</sup>

Apart from the substantial difference in the platinum chemical shift, the protonation of the oxygen atom in the platinum coordination sphere of the pentacyano species causes other significant changes in NMR and Raman parameters as can be seen from Tables 1 and 2, respectively.

**Characteristics of the  $[\text{Pt}(\text{CN})_5\text{X}]^{2-}$  Species.** The data for the  $[\text{Pt}(\text{CN})_5(\text{H}_2\text{O})]^-$  and  $[\text{Pt}(\text{CN})_5(\text{OH})]^{2-}$  species can be

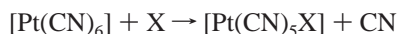
(50) In the recent paper<sup>19</sup> a  $[\text{Pt}^{\text{IV}}(\text{CN})_5\text{Cl}]^{2-}$  complex formed in the solution due to impurity of chloride ion was mistakenly assigned to a hitherto unknown  $[\text{Pt}^{\text{IV}}(\text{CN})_5(\text{H}_2\text{O})]^-$  ion.

(51) (a) Above, we mentioned that redox decomposition of the  $[(\text{NC})_5\text{-PtTlCN}]^-$  species results in formation of both hexa- and pentacyano species of platinum(IV) in solution. Different ratios between  $[\text{Pt}(\text{CN})_6]^{2-}$  and  $[\text{Pt}(\text{CN})_5(\text{H}_2\text{O})]^-/([\text{Pt}(\text{CN})_5(\text{OH})]^{2-})$  complexes can be produced depending on the experimental conditions, especially on the CN<sup>-</sup> content of the bimetallic Pt–Tl complexes. It turned out that change of the cyanide concentration and/or of the acidity of the solution after the redox reaction had no influence on the ratio between the two platinum species for any of the studied solutions:  $c_{\text{CN}} = 0\text{--}0.08$  M,  $\text{pH} = 1.2\text{--}9.2$ ,  $[\text{Pt}(\text{CN})_5(\text{H}_2\text{O})]^- = 0.03$  M. We suppose that this can be attributed to the kinetic inertness regarding coordination of the sixth cyanide ion to the platinum atom. It was also shown that the reaction between pentacyanoiodide complex of platinum(IV) and cyanide is slow and formation of hexacyano species is usually not complete while it is considerably accelerated and results in practically quantitative transformation into  $[\text{Pt}(\text{CN})_6]^{2-}$  when the solution was irradiated.<sup>3,8,51</sup> This is a usual situation for cyano complexes of transition metals where the last stage in the stepwise formation of  $[\text{M}(\text{CN})_6]^{n-}$  complexes from aqua cations is the slow one.<sup>1</sup> The break of the Pt–Tl bond can be assumed to activate fast cyanide transfer reaction from the thallium to the platinum atom leading to a “decomposition equilibrium” between penta- and hexacyano complexes of platinum(IV) while the further formation of  $[\text{Pt}(\text{CN})_6]^{2-}$  is kinetically hindered. (b) Babkov, A. V. *Dokl. Akad. Nauk* **1981**, *261*, 889–891.

correlated with their halide analogues [Pt(CN)<sub>5</sub>X]<sup>2-</sup> (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>). Vibrational spectra of pentacyanohaloplatinate(IV) complexes both in solid and in aqueous solution were fully described by Memering et al.,<sup>15</sup> and the fundamental frequencies were assigned. Both [Pt(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>-</sup> and [Pt(CN)<sub>5</sub>(OH)]<sup>2-</sup> complexes possess the same molecular symmetry of point group C<sub>4v</sub> as the [Pt(CN)<sub>5</sub>X]<sup>2-</sup> (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) anions; this results in similarity of their vibrational spectra (cf. Raman spectra of the aqueous solutions of [Pt(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>-</sup> and [Pt(CN)<sub>5</sub>(OH)]<sup>2-</sup>, Table 2). In the same way as for the pentacyanohalide species, the patterns observed in the most informative cyanide stretching region of [Pt(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>-</sup> and [Pt(CN)<sub>5</sub>(OH)]<sup>2-</sup> exhibit A<sub>1</sub> and B<sub>1</sub> vibrations of only equatorial cyano ligands at about 2200 cm<sup>-1</sup>. The planar A<sub>1</sub> (Pt–C) stretching mode corresponds to a band at 464 cm<sup>-1</sup>. As one would expect, the Pt–O stretching vibration is significantly shifted to higher frequencies compared to the Pt–X (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) and exhibits bands at 546 and 630 cm<sup>-1</sup> for the OH<sup>-</sup> and H<sub>2</sub>O ligands, respectively.

In contrast to the vibrational data, a complete NMR characterization of the complexes, [Pt(CN)<sub>5</sub>X]<sup>2-</sup>, (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, H<sub>2</sub>O, OH<sup>-</sup>) has not been reported.<sup>52</sup> In the present work, we have prepared pentacyanohalides of platinum(IV) in aqueous solution and obtained a full set of their <sup>13</sup>C and <sup>195</sup>Pt NMR parameters (Table 1). <sup>195</sup>Pt NMR chemical shifts of these complexes cover a wide range (about 1400 ppm, cf. Table 1) which can be attributed to the well-known sensitivity of the <sup>195</sup>Pt nucleus to the chemical environment.<sup>25,26</sup>

Also other NMR parameters for the [Pt<sup>IV</sup>(CN)<sub>5</sub>X] species vary with X (Table 1). The most pronounced difference is observed for the <sup>13</sup>C NMR chemical shift (δ<sub>transC</sub>) and <sup>195</sup>Pt–<sup>13</sup>C spin–spin coupling constants of the apical cyano ligand. This is best rationalized in terms of a substantial *trans* influence of the X ligand which is well-known for a large number of σ-bonded complexes of transition metals. Considering the substitution reaction



the “sign” of the *trans* influence depends on the donor ability of the X ligand. Thus, coordination of a ligand with strong acceptor (or weak donor) ability should cause strengthening of the Pt–CN<sub>trans</sub> bond as compared to [Pt(CN)<sub>6</sub>]<sup>4-</sup>,<sup>53a</sup> thus affecting the <sup>1</sup>J(Pt–C) values of the halide derivatives<sup>53b</sup> (Table 1). In the series of pentacyano complexes of tetravalent platinum presented, the water ligand exhibits the largest <sup>1</sup>J(Pt–CN<sub>trans</sub>) coupling constant.

Oligonuclear Pt–Ti and Pt–Pt cyano compounds can also be viewed as [Pt(CN)<sub>5</sub>X] species in which X = Ti, Ti(CN)<sub>m</sub> (m = 1–3), and Pt(CN)<sub>5</sub>, respectively. Several of the complexes demonstrate opposite sign of the *trans* influence resulting in weakening of the Pt–CN<sub>trans</sub> bond (Table 1). This can be attributed to varying donor ability of the X ligand: the lowest

value of <sup>1</sup>J(Pt–C<sub>trans</sub>) occurs for the covalent Pt–Pt bond in the [Pt(CN)<sub>5</sub>]<sub>2</sub> species.

## Conclusions

Formation of a stable Pt(CN)<sub>5</sub> entity seems to be a common and overlooked feature of the coordination chemistry of platinum in oxidation states III and IV. Apart from the substitution reactions of [Pt<sup>IV</sup>X<sub>6</sub>]<sup>2-</sup> or [Pt<sup>IV</sup>(CN)<sub>4</sub>X<sub>2</sub>]<sup>2-</sup> (X = halide) with cyanide, pentacyano complexes can be obtained from oxidative addition reactions of [Pt<sup>II</sup>(CN)<sub>4</sub>]<sup>2-</sup> with either ICN, BrCN, or [Ti(CN)<sub>n</sub>]<sup>3-n</sup> (n = 1–4). In the latter case, bimetallic complexes [(NC)<sub>5</sub>Pt–Ti(CN)<sub>n</sub>]<sup>n-</sup> (n = 0–2) or the trimetallic [(NC)<sub>5</sub>Pt–Ti–Pt(CN)<sub>5</sub>]<sup>3-</sup> form as stable intermediates; they provide a route to hitherto unknown pentacyano complexes of tetravalent ([Pt(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>-</sup> and [Pt(CN)<sub>5</sub>(OH)]<sup>2-</sup>) and trivalent ([Pt(CN)<sub>5</sub>–Pt–Pt(CN)<sub>5</sub>]<sup>4-</sup>) platinum. In all these cases, the platinum atom is hexacoordinated. The sixth position in the coordination sphere of the metal can be occupied by different types of anionic (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, OH<sup>-</sup>), molecular (H<sub>2</sub>O), or “metal” (Ti, Ti(CN)<sub>m</sub> (m = 1–3), Pt(CN)<sub>5</sub>) ligands. In all the pentacyano complexes a pronounced *trans* influence appears as a substantial difference between the <sup>195</sup>Pt–<sup>13</sup>C spin–spin coupling constant for the apical and equatorial carbon sites. The X ligands in the tetravalent platinum species [Pt(CN)<sub>5</sub>X] can be positioned in a series of decreasing <sup>195</sup>Pt–<sup>13</sup>C<sub>trans</sub> coupling constant: H<sub>2</sub>O > Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup> > OH<sup>-</sup> > CN.

The binuclear species [(NC)<sub>5</sub>Pt–Pt(CN)<sub>5</sub>]<sup>4-</sup> is a rare representative of unbridged dimeric complexes of trivalent platinum; it is the first example of a homoligand bis-platinum compound. This is also the first example where a Pt<sup>III</sup>–Pt<sup>III</sup> complex was obtained through oxidation of the monomeric square-planar platinum(II) species by a metal complex ([Ti<sup>III</sup>(CN)<sub>2</sub>]<sup>+</sup>). Charge transfer between the Pt<sup>II</sup> and Ti<sup>III</sup> species yields Ti<sup>+</sup> and a Pt–(III) dimer; it is possible that also reactions of tin(IV) and lead(IV), which have two oxidation states with two electrons between, can yield Pt(III) compounds.

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**Supporting Information Available:** Iterations/simulations of NMR spectra, and <sup>13</sup>C and <sup>195</sup>Pt NMR spectra for the pentacyano complexes are available (12 pages). Ordering information is given on any current masthead page.

IC980186R

(52) Some <sup>13</sup>C and <sup>195</sup>Pt NMR parameters for the species [Pt(CN)<sub>5</sub>X]<sup>2-</sup> (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) in solution have been reported previously.<sup>13,16</sup>

(53) (a) Levin, A. A.; Dyachkov, P. N. *Electronic Structure, Geometry, Isomerism and Transformations in Heteroligand Molecules*; Nauka: Moscow, 1990; p 256. (b) Assuming that s-electron contribution to the spin–spin coupling is not significantly affected in this series of [Pt(CN)<sub>5</sub>X] compounds, cf. ref 19.