1. Introduction and objectives

Tandem complex formation and redox reactions (occasionally together with hydrolysis) are typical feature of the systems, which have been investigated through this thesis. This complexity throughout is what makes it to be a great challenge to work in the field of thallium chemistry. However, not so many laboratories work with thallium owing to its toxicity, especially when it is in combination with hydrogen–cyanide. I feel myself lucky to have the opportunity to work in an international group dealing with thallium chemistry at Debrecen University and also at The Royal Institute of Chemistry in Stockholm.

The Tl^I–Tl^{III} relationship is a dominant feature of thallium chemistry. The standard reduction potentials at 25°C and unit activity of H$^+$ are: Tl^I/Tl = –0.336 V, Tl^{III}/Tl = +0.72 V, and Tl^{III}/Tl^I = +1.25 V. Estimates have also been made for the couples Tl^{III}/Tl^{II} = +0.33 V and Tl^{II}/Tl^I = 2.22 V. The generally valid limitations concerning the use of standard electrode potentials to predict the redox chemistry of 'real' systems are especially important in the case of thallium: factors such as complex formation in the presence of coordinating anions or neutral ligands and pH dependence due to hydrolysis do affect the actual or formal redox potentials.

A good example for this situation, that Tl^{III} does not easily oxidize cyanide in contrast to general assumptions based on the standard reduction potentials of the Tl^{III}/Tl^I (E^o = 1.25 V), and $(CN)_2$/CN^- or $(CN)_2$/HCN (E^o = 0.27 V and 0.37 V for CN^- and HCN, respectively) redox couples. It has been shown that thallium(III) forms kinetically stable cyanide complexes in aqueous solution. Reduction of thallium(III) to thallium(I) is found to be limited in the solutions under studied conditions (50 mM thallium, CN/Tl $\leq$ 6 and high acidity, room temperature) during a period of one year but it is increased for CN/Tl > 6 and pH > 4. In contrast to Tl^{III}, Tl^I does not form complexes with cyanide.

The complexes with composition $[Tl^{III}(CN)_n(aq)]^{3-n}$ (n = 1–4) can be formed in aqueous solution by addition of NaCN to the aqueous solution of $Tl(ClO_4)_3$ and adjusting CN^-/Tl^{III} ratio and pH. Formation constants of these species are stronger

than any other known thallium(III) complexes with monodentate ligands. Structural information on the $[Tl^{III}(CN)_n(aq)]^{3-n}$ species in aqueous solution obtained from a combination of EXAFS, LAXS and vibrational spectroscopy techniques.

Surprisingly, no solid–state structures of homoligand $Tl(CN)_4^-$ and $Tl(CN)_3$ species has been yet reported. The only known homoligand thallium cyanide compound in solid state is "$Tl(CN)_2$", prepared by Fronmuller in 1878. The compound is assumed to have the mixed valenced, $Tl^I Tl^{III}(CN)_4$ composition.

The chemistry of metal–metal bonded compounds has generated substantial interest during the last two decades. Important properties of these complexes range from catalytic activity through unusual magnetic or optical properties to their application as precursors in synthesis. Our group have reported the synthesis and structural features of four binuclear platinum–thallium cyano compounds containing a direct and unsupported by ligands metal–metal bond. The complexes, prepared in a direct reaction between $Pt(CN)_4^{2-}$ and $Tl(CN)_n^{3-n}$ in aqueous solution, are found to be surprisingly stable under certain conditions in spite of the strong oxidative properties of thallium(III). The structure of the products represented by the formula $[(NC)_5Pt–Tl(CN)_n]^{n-}$ (n = 0–3) have been determined by means of multinuclear NMR (^{195}Pt, ^{205}Tl, ^{13}C) and supported by Raman spectroscopy. In addition, a trinuclear complex with the formula $[(NC)_5Pt–Tl–Pt(CN)_5]^{3-}$ has been prepared in aqueous solution via reversible reactions. The general equation of the formation can be written as follows:

$$mPt(CN)_4^{2-} + Tl(CN)_n^{3-n} \rightleftharpoons [Pt_mTl(CN)_{4m+n}]^{(3-2m-n)}$$
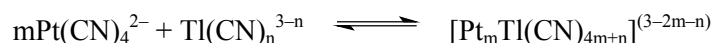
EXAFS studies of the complexes confirm short Pt–Tl bond lengths (2.60–2.63 Å) both in solution and solid phase and allow also to establish the presence of water molecules which are coordinated to the thallium center together with cyanide ligands and a platinum atom.

The common structural features of the complexes are the metal–metal bond and the octahedral geometry of platinum, which is bound to five cyanide ligands and the thallium center. Both axial and equatorial cyanides of the Pt–centre are stable thermodynamically and very inert kinetically in ligand exchange reactions. All our attempts to form similar complexes with different metal centers or other ligands

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instead of the cyanides bound to platinum failed so far. On the other hand, the labile cyanides connected to the Tl–center can be substituted with O– or N–donor ligands and with aminopolycarboxylates (APCs, i.e.: methyliminodiacetate, nitrilotriacetate, and ethylenedinitrilotetraacetate). Thus the solid $[(CN)_5Pt–Tl]_{(s)}$ can be dissolved in water containing 1 equivalent APC:

$$[(CN)_5Pt–Tl]_{(s)} + APC \rightarrow [(CN)_5Pt–Tl(APC)]$$
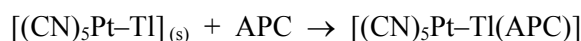
The metal–metal bonded complexes, could be characterized by NMR in solution (in the case of mimda, nta and edta) and with X–ray diffraction in the solid phase (in the case of nta). The $[(CN)_5Pt–Tl(edta)]^{4-}$ can also be prepared by the reaction of $Tl(edta)(CN)^{2-}$ with $Pt(CN)_4^{2-}$.

$$Pt(CN)_4^{2-} + Tl(edta)(CN)^{2-} \rightleftharpoons [(CN)_5Pt–Tl(edta)]^{4-}$$
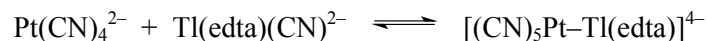
The aim of this work was to characterize the structure of some thallium–cyanide complexes and to give an insight into the kinetics and mechanism of the formation of novel metal–metal bonded complexes.

2.   Applied methods and equipments

Concentrated (1.2 M) aqueous solution of $Tl(ClO_4)_3$ in 4.9 M $HClO_4$ was obtained by anodic oxidation of $TlClO_4$. The thallium(III) concentration was determined by bromatometric titration. The $Tl^{III}–CN^-–H_2O$ solutions were prepared by addition of a calculated volume of a sodium cyanide solution to the stock solution of thallium(III) perchlorate.

pH values were measured by combination of electrodes (Radiometer GK2401B or Metrohm, 6.0234.100) connected to a pH–meter (Radiometer PHM26 or PHM62 or PHM84). The pH–meter was calibrated using the method of Irving et al. The pH corresponds to $–\log[H^+]$ through this paper.

NMR spectra were recorded with Bruker Avance360, Bruker AM400 and Bruker DMX500 spectrometers with probe temperature of 25 (±0.5) ^{o}C. Integrals could be used for calculations of concentrations of species in all cases.

Crystallographic data were collected on KappaCCD and Enraf–Nonius CAD4 diffractometers using λ (Mo K$_\alpha$, 0.71073)

Kinetic measurements were made mainly with a CARY 1E UV–Visible spectrophotometer and with an Applied Photophysics DX–17 MV stopped–flow instrument, using 1cm, 0.1cm, 0.02cm and 0.001cm wide optical cells. The temperature was set to 25 ºC in all cases and controlled by a LAUDA RM 20 thermostat. The solutions contained 1 M NaClO$_4$ as ionic medium. The kinetic curves were fitted with an Origin (Microcal) routine, and all experimental rate constants were evaluated simultaneously with Scientist (Micromath) data analysis program.

3.   Results

We have studied: i) the kinetics and mechanism of platinum–thallium bonded complexes, and ii) the solid structure of several Tl^{III}–cyanide complexes. Structural informations are essential for mechanistic considerations.

3.1   Structural studies.

3.1.1 Homoligand Tl(CN)$_4^-$ and for the first time Tl(CN)$_3$ species has been synthesized in the solid state and their structures have been solved by single crystal X–ray diffraction method. Interesting redox processes have been found between Tl^{III} and CN$^-$ in non–aqueous solution and in Tl$_2$O$_3$ – CN$^-$ aqueous suspension. The redox reactions are terminated, when all thallium is present in form of Tl^I (50 %, product of reduction) and the [Tl(CN)$_4$]$^-$ complex (50 %, product of complex formation). Two crystalline compounds Tl^I[Tl^{III}(CN)$_4$] (**2**) and Tl$^I_2$C$_2$O$_4$ (**5**) have been obtained as products of the redox reactions and their structures determined by X–ray diffraction method.

3.1.2 The Tl(CN)$_3$ species has selectively been extracted from aqueous solution containing CN$^-$/Tl^{III} = 3 to diethyl ether. Depending on the water content in the ether phase, Tl(CN)$_3$·H$_2$O (**1**) or Tl^I[Tl^{III}(CN)$_4$] (**2**) crystals can be prepared from

water saturated or dried solvent, respectively. In the crystal structure of Tl(CN)$_3$·H$_2$O (**1**) complex, the thallium(III) ion has a trigonal bypiramidal geometry with three cyanides in the trigonal plane, while an oxygen atom of the water molecule and a nitrogen atom from a cyanide ligand, attached to a neighboring thallium complex form a linear O–Tl–N fragment. Cyanide ligand bridges thallium units in a infinite zigzag–wise chain structure.

3.1.3 M[Tl(CN)$_4$] (M = K, Na) can easily be crystallized from their aqueous solutions. Compounds Tl^I[Tl^{III}(CN)$_4$] (**2**) and K[Tl(CN)$_4$] (**3**) are isostructural. Their structure is a derivative of Scheelite–type structures, where thallium(III) has nearly tetrahedral environment of carbon atoms, while nitrogen atoms occupy practically ideal cubic positions in the polyhedra of thallium(I) and potassium.

3.1.4 In contrast to the thallium(I) and potassium salts of the [Tl(CN)$_4$]$^-$ anion, coordination environment of sodium atoms in the Na[Tl(CN)$_4$]·3H$_2$O (**4**) is a pseudooctahedron. The *fac*–[NaN$_3$O$_3$] polyhedron is built by nitrogen atoms of cyanides and water molecules.

In spite of the fact that among the thallium(III) tetracyano compounds, the isostructural M[Tl(CN)$_4$] (M = Tl and K) ((**2**)and (**3**) respectively) and the Na[Tl(CN)$_4$]·3H$_2$O (**4**) crystallize in different crystal systems, thallium(III) ion has the same tetrahedral geometry in the [Tl(CN)$_4$]$^-$ unit.

3.2 Kinetic studies.

As a continuation of our structural and equilibrium studies on the unusual platinum–thallium bonded cyano–compounds, detailed kinetics of the [(CN)$_5$PtTl(CN)$_3$]$^{3-}$, [(CN)$_5$Pt–Tl(CN)]$^-$, [(CN)$_5$Pt–Tl–Pt(CN)$_5$]$^{3-}$ and [(CN)$_5$Pt–Tl(edta)]$^{4-}$ complexes have been evaluated.

3.2.1 The Pt–Tl bonded cyano complexes are formed from Pt(CN)$_4^{2-}$ and Tl(CN)$_n^{3-n}$ reactants via very similar reaction paths. The overall reaction includes *i*) metal–metal bond formation and *ii*) the coordination of a fifth cyanide ion to Pt. The order of these two steps is undoubtedly established in the formation of [(CN)$_5$Pt–Tl–Pt(CN)$_5$]$^{3-}$. It is most likely that the same sequence is valid in the formation of [(CN)$_5$Pt–Tl(CN)]$^-$ and [(CN)$_5$Pt–Tl(CN)$_3$]$^{3-}$, i.e. the metal–metal bond formation is the first step. It is a partial electron transfer reaction, which

reduces the electron density of, and enhances nucleophilic attack at the Pt center. The corresponding reactions are different in the nucleophilic agent, which donates the fifth cyanide to Pt.

3.2.2 In the alkaline–slightly acidic pH range CN^- catalyzes the formation of the $[(CN)_5Pt–Tl(CN)_3]^{3-}$ and HCN has negligible effect even when it is present at considerably higher concentrations than CN^-. This difference in the kinetic behavior is in line with the fact that CN^- is a much stronger nucleophile than HCN and strongly suggests that step *ii*) is a nucleophilic addition.

3.2.3 The concentration of CN^- is very low at pH ~ 2 and $Tl(CN)_2^+$ is the nucleophilic agent in the formation of $[(CN)_5Pt–Tl(CN)]^-$. Although HCN is present at comparable concentrations to $Tl(CN)_2^+$, it does not affect the complex formation kinetics. To some extent it is surprising that $Tl(CN)_2^+$ is more reactive (virtually it is a stronger nucleophile) than HCN. The noted difference can be understood by considering that the attractive electrostatic interactions between the negatively charged $[(CN)_4Pt\cdots Tl(CN)_2]^-$ intermediate and the positively charged $Tl(CN)_2^+$ promote their interaction. Such an enhancement is absent with HCN.

3.2.4 The results for the formation of the trinuclear $[(CN)_5Pt–Tl–Pt(CN)_5]^{3-}$ complex confirm that HCN can also act as a nucleophilic agent and donate a cyanide ligand to the Pt–center. In this case, other nucleophiles are present at very low concentration levels and the reaction occurs with HCN simply because it is present in sufficiently large concentration.

3.2.5 The $[(CN)_5Pt–Tl(edta)]^{4-}$ complex, having direct metal–metal bond has been prepared in solution by two different reactions: a) dissolution of $[(CN)_5Pt–Tl]_{(s)}$ in aqueous solution of edta ligand, b) from $Pt(CN)_4^{2-}$ and $Tl(edta)(CN)^{2-}$ reactants.
3.2.5.1 The decomposition reaction is greatly accelerated by cyanide and significantly inhibited by edta. It proceeds through the $[(CN)_5Pt–Tl(CN)_3]^{3-}$ intermediate. This complex decomposes to $Pt(CN)_4^{2-}$ and $Tl(CN)_4^-$. To complete the reaction $Tl(CN)_4^-$ and $edta^{4-}$ react in relatively fast equilibrium step(s) giving $Tl(edta)(CN)^{2-}$.

3.2.5.2 The formation of $[(CN)_5Pt–Tl(edta)]^{4-}$ complex can proceed via two different pathways. An 'indirect path' is dominant without suppression of the $[Tl(CN)_4^-]$ in the absence of excess edta, although $Tl(CN)_4^-$ is only minor species

in the solution of the $Tl(edta)(CN)^{2-}$ reactant. When the equilibrium concentration of $Tl(CN)_4^-$ is suppressed by addition of edta to the $Tl(edta)(CN)^{2-}$ reactant, another 'direct' path becomes kinetically significant. First an $[(CN)_4Pt\cdots Tl(CN)(edta)]^{4-}$ intermediate is formed followed by the release of the cyanide from the Tl–centre and the third, rate determining step is the coordination of a cyanide from the bulk to the Pt–centre of the intermediate. This significant difference in the sequence of the cyanide coordination to the platinum center and the release of the cyanide(s) from thallium center compared to the studied parent Pt–Tl–bonded cyano complexes (*vide supra*) might be the consequence of the bulky edta ligand in the coordination sphere.

4. Possible application of the results

The results presented here are of basic research. Therefore indirect application during some similar projects can be expected.

Our metal–metal bonded complexes are found to be feasible precursors in the synthesis of some other hitherto unknown complexes (for example Pt^{IV}–pentacyano, or Pt^{III}–Pt^{III} bonded cyanides). Electro–, photochemical, photophysical characterization of these compounds or derivatives can clear in the future, if they are feasible as 'light-harvesting' material.

5. Scientific publications of Péter Nagy

(in reverse chronological order)

Papers involved in the dissertation:

4 Péter Nagy, Andreas Fischer, Julius Glaser, Andrey Ilyukhin, Mikhail Maliarik and Imre Tóth
Solubility, Complex formation and Redox Reactions in the Tl_2O_3–HCN/CN^- –H_2O, Tl^{III}–CN^-–$(C_2H_5)_2O$/H_2O Systems. Crystal Structures of the Cyano compounds: $Tl^I[Tl^{III}(CN)_4]$, $Na[Tl(CN)_4]\cdot3H_2O$, $K[Tl(CN)_4]$, $Tl(CN)_3\cdot H_2O$; and $Tl^I_2C_2O_4$
(manuscript)

3 Péter Nagy, Róbert Jószai; István Fábián; Imre Tóth; Julius Glaser
The Decomposition and Formation of the Platinum–Thallium Bond in the $[(CN)_5Pt–Tl(edta)]^{4-}$ Complex. Kinetics and Mechanism.
Journal of Molecular Liquids (special issue for the 28th International Conference on Solution Chemistry)*, (accepted for publication)*

2 Péter Nagy, Imre Tóth; István Fábián; Mikhail Maliarik; Julius Glaser
Kinetics and Mechanism of Platinum–Thallium Bond Formation: The Binuclear $[(CN)_5Pt–Tl(CN)]^-$ and the Trinuclear $[(CN)_5Pt–Tl–Pt(CN)_5]^{3-}$ complex
Inorganic Chemistry (accepted for publication)

1 Péter Nagy, Imre Tóth; István Fábián; Mikhail Maliarik; Julius Glaser.
Kinetics and Mechanism of Formation of the Platinum–Thallium Bond: The $[(CN)_5Pt–Tl(CN)_3]^{3-}$ Complex.
Inorganic Chemistry **2003**, *42*, 6907–6914.

Paper not invoved in the dissertation:

1 Róbert Jószai; Péter Nagy; Imre Tóth; Attila Bényei; Andreas Fischer and Andrey Shchukarev.
Metal–metal bond or isolated metal centers? Reaction of $Hg(CN)_2$ with square planar transition metal cyanides
(manuscript in preparation)

Lectures and posters presented at meetings

13. Imre Tóth, **Péter Nagy**, István Fábián, Mikhail Maliarik and Julius Glaser
    Kinetic studies of direct Pt–Tl bonded cyano–complexes
    Inorganic Reaction Mechanisms Meeting, Athens, Greece **2004**. (lecture)

12. **Péter Nagy**, Róbert Jószai, Imre Tóth, István Fábián and Julius Glaser
    Kinetics and mechanism of formation and decomposition of $(CN)_5Pt–Tl(Hedta)^{4-}$
    Inorganic Reaction Mechanisms Meeting, Athens, Greece **2004**. (poster)

11. **Péter Nagy**, Imre Tóth, István Fábián, Mikhail Maliarik and Julius Glaser
    Formation Kinetic Studies of Pt–Tl Bonded Cyano–Complexes
    International Conference on Solution Chemistry, Debrecen, Hungary **2003**. (lecture)

10. **Péter Nagy**, Imre Tóth, Béla Győri, Attila Bényei, Mikhail Maliarik and Andrey Ilyukhin
    Preparation and Structural Characterization of Thallium(I) and Thallium(III) Cyano–Complexes
    XXXVIII. Coordination Chemistry Conference, Gyula, Hungary **2003**. (lecture in Hungarian)

9. **Péter Nagy**, Róbert Jószai, István Fábián and Imre Tóth
    Formation Kinetic Studies of $[(CN)_5Pt–Tl(edta)]^{4-}$
    Inorganic Mechanisms Discussion Group, Newcastle, England **2003**. (poster)

8. Róbert Jószai, **Péter Nagy**, Imre Tóth, István Fábián, Michail Maliarik and Julius Glaser
    Structural Characterization of Direct Pt–Tl Bonded Complexes
    4th Central European NMR Symposium and 4th Central European Bruker NMR Users Meeting, Budapest, Hungary **2002**. (poster)

7. Imre Tóth, Róbert Jószai, **Péter Nagy**, István Fábián, Mikhail Maliarik, Julius Glaser
    Naked Tl–Pt Bonded Small Cyano Clusters: Results and Question Marks
    Inorganic Chemistry EuroConference on the Inorganic Side of Molecular Architecture, San Feliu de Guixols, Spain **2002**. (poster)

6. **Péter Nagy**, Róbert Jószai, István Fábián and Imre Tóth
    Kinetic Studies of the $[(CN)_5Pt–Tl(edta)]^{4-}$ Complex
    XXXVII. Coordination Chemistry Conference, Mátraháza, Hungary **2002**. (lecture in Hungarian)

5. **Péter Nagy**, Imre Tóth, István Fábián and Julius Glaser
    Formation Kinetic Studies of Direct Pt–Tl Bonded Cyano–Complexes
    Dalton Discussion 4. Kloster Banz, Germany **2002**. (poster)

4. **Péter Nagy**, Imre Tóth, István Fábián and Julius Glaser
    Formation Kinetic Studies of Direct Pt–Tl Bonded Cyano–Complexes

14th International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Veszprém, Hungary **2001**. (poster)

3. **<u>Péter Nagy</u>**, Imre Tóth, István Fábián and Julius Glaser
   Formation Kinetic Studies of Cyano–Complexes Containing one or two Direct Pt–Tl Bond
   XXXV. Coordination Chemistry Conference, Kecskemét, Hungary **2000**. (lecture in Hungarian)

2. **<u>Péter Nagy</u>**, Imre Tóth
   Formation Kinetic Studies of Pt–Tl bond
   XXIV. National Scientific Conference and Competition for Undergraduate Students, Veszprém, Hungary **1999**. (lecture in Hungarian)

1. István Bányai, István Fábián, Julius Glaser, **Péter Nagy and** <u>Imre Tóth</u>
   Formation Kinetic Studies of Pt–Tl bond
   XXXIII. Coordination Chemistry Conference, Tata, Hungary **1999**.
   (lecture in Hungarian)