



**MULTINUCLEAR NMR STUDIES OF THE STRUCTURE
AND FLUXIONALITY FOR THE Al(III)- AND Ti(III)-
AMINOPOLYKARBOXYLATE COMPLEXES AND
SOME METAL-METAL BONDED COMPOUNDS
FORMED BY Ti(III) AND TRANSITION METAL
CYANIDES**

Propositions of Ph.D. thesis

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1. INTRODUCTION

Aluminium, having an abundance of 8.3% of weight, is the commonest metallic element in the Earth's crust. It occurs widely in igneous minerals such as feldspars and micas. Metal aluminium is used widely in different major areas like building and construction, containers and packing, transportation, electric conductors, machinery and equipment. Aluminium contamination and mobility in the environment has attracted considerable attention in recent times because of the acidification of natural waters and soils arising from acid rain. The abnormally high aluminium level in humans has been linked to important pathologies. The solubility and transport is greatly increased by complex formation. As a "hard" metal ion, Al^{3+} has high affinity to "hard" donor ligands such as O-containing compounds. These ligands are widely found in geochemical, biological and industrial systems.

For studying the chemistry of different Al(III) systems a proper experimental technique is required. Finding a good method might be an easier problem for some other metals, but aluminium is a "hard metal" in this way also. Owing to the electronic structure of $1s^2 2s^2 2p^6$ and the absence of extended delocalised electronic structure in most of the ligands, UV-VIS spectroscopy is useless. There are no oxidation-reduction processes in these systems, so application of redox potential measurements is dropped. Regarding to the slow formation reactions the potentiometric methods can be very time consuming, still this is the way how most equilibrium constants are determined. Aluminium is "silent" in ESR. Although ^{27}Al is a 100% abundant NMR nucleus having a quadrupolar moment ($I = 5/2$), in the most cases no information can be obtained from the observed very broad signals. Therefore, it is very useful if studies can be performed from the side of the ligand (*e.g.* ^1H , ^{13}C , ^{19}F NMR).

The provisional name of thallium, from the Greek *θαλλός*, or Latin *thallos*, a budding twig – a word which is frequently employed to express the beautiful green tint of young vegetation. Mendeleev placed the element to the end of Group

III, and it has remained there ever since. Element 81 is a white soft metal with melting point 302 °C, and $\rho = 11,85 \text{ g/cm}^3$. Chemistry of thallium was not the most effectively explored field in the last decades, probably because of the overwhelmed toxicity diffused by the famous *Agatha Christie* novel: *The Pale Horse*. It is not so rife in practice, but has some use: e.g. thallium is added in small amounts to glass in order to increase the density and refractive index.

NMR spectroscopy is a superior method in thallium chemistry, because both stable isotopes, ^{205}Tl (70,5%) and ^{203}Tl (29,5%) have $I = 1/2$ spin nuclei. ^{205}Tl nuclei is quite sensitive (the proportion is 0.13 referred to ^1H NMR) and has a wide chemical shift range, which indicates fine chemical differences.

Chemistry of metal-metal bonded compounds deserved substantial interest during the last two decades, because of the valuable properties of these complexes ranging from catalytic activity through unusual magnetic or optical properties to their application as precursors in synthesis. The Tl(III)/Tl(I) – Pt(II)/Pt(IV) redox reactions are the main parts of two-electron transfer models. Both platinum and thallium have been shown to mediate net two-electron transfer in many redox processes. Some Pt compounds (e.g. $\text{K}_{1,75}\text{Pt}(\text{CN})_4 \cdot 1,5\text{H}_2\text{O}$) may form one dimensional wires.

2. AIMS AND EXPERIMENTAL METHODS

The aim of this thesis is to collect structural, equilibrium and fluxionality data of Al(III) és Tl(III) complexes. We shortly summarize here the experimental methods used for the particular systems as follows.

We report here results for the Al(III) – edphp²⁻ (etiléndiamine-N,N'-bis-3-hidroxy-2-propionate) – H⁺ system. The aim of this study is to elucidate the equilibrium and the structure both in solution and for the solids using pH-potentiometry, ^1H and ^{27}Al NMR, Electro Spray Ionization Mass Spectroscopy (ESI MS) and single-crystal X-ray diffraction methods.

The $M(\text{edta})^-$ systems ($M = \text{Al}, \text{Ga}$ and In) in solution have been reinvestigated while varying the temperature, pH or using different solvents in order to change the rate of the fluxionality. Structures and relative stabilities of various forms of $\text{Al}(\text{edta})^-$ involved in carboxylate exchange processes have also been examined using ^1H , ^{13}C and ^{27}Al NMR and density functional theory calculations.

The $[(\text{CN})_5\text{Pt}-\text{Tl}(\text{APK})]$ complexes have been prepared in solution by reaction of $[(\text{CN})_5\text{Pt}-\text{Tl}(\text{s})]^0$ with different aminopolycarboxylate ligands. The properties of these complexes have been studied by UV-VIS and multinuclear NMR spectroscopy, X-ray diffractions and DFT calculations.

In the last part of the thesis we deal with the study of interaction between $\text{K}_2[\text{M}(\text{CN})_4]$ ($M = \text{Ni}(\text{II}), \text{Pt}(\text{II}), \text{Pd}(\text{II})$) and $\text{Hg}(\text{CN})_2$ in aqueous solutions by using UV-VIS and multinuclear NMR spectroscopy. The main methods used for study in the solid state are the electron microscopy, Raman, time resolved luminescence spectroscopy, XPS and single crystal X-Ray in order to get information about structure and bonding.

3. SUMMARY OF NEW RESULTS.

3.1. The equilibrium and the structure of the complex formed by **Al(III) and ethylenediamine- N,N' -bis 3-hydroxy-2-propionate** (edbhp^{2-}) have been studied using pH-potentiometry, ^1H and ^{27}Al NMR, ESI MS and single crystal X-ray diffraction methods. The **edbhp ligand is a strong Al-binder** in aqueous solution for pH between 4 and 8 and for $c_{\text{Al}} = c_{\text{EDBHP}} \geq 0.1 \text{ mmol/dm}^3$. The dominating complex identified by ESI MS and potentiometry is a neutral dimer, $\text{Al}_2\text{L}_2(\text{OH})_2$, with $\log \beta_{22-2} = 14.16 \pm 0.03$. In the solid **$\text{Al}_2(\text{edbhp})_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$** the Al(III) ions are connected through a double hydroxo bridge. Both four-dentate organic ligands are coordinated terminally through two carboxylate groups and two N donors forming three five-membered chelate rings. The hydroxyl groups of the ligand edbhp remain protonated and are not coordinated to the aluminium ions. The

structure and composition of the dimer are very likely the same in solution and the solid state. (Paper 3.)

3.2. Multinuclear NMR studies of $M(\text{edta})^-$ complexes ($M = \text{Al, Ga and In}$) by ^1H , ^{13}C and ^{27}Al NMR in solution while varying the temperature, pH or using different solvents have been done. The features of the high field NMR spectra show that the complexes have **similar structure in solution and solid state, i.e. the Al(III) and Ga(III) are octahedrally coordinated** by the hexadentate edta ligand. In the case of the octahedral Al(III) and Ga(III) complexes the fluxional rearrangement of the chelate rings can be followed by ^1H and ^{13}C NMR. The *indirect exchange* between the *axial* and *equatorial* acetate arms of $\text{Al}(\text{edta})^-$, located at different N-atoms of the ligand, and the *turning of ethylene group* could be a proton catalysed reaction assisted with water molecule(s). We have determined the rate constants and the activation parameters for these two (coupled) intramolecular rearrangements. The turning of ethylene group is faster ($\Delta H^\ddagger = 33,1 \pm 2,8 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -110 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$, a $\log k_{298} = 1,30 \pm 0,48$) compared to the *exchange* between the *axial* and *equatorial* acetate arms ($\Delta H^\ddagger = 60 \pm 4 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -25 \pm 21 \text{ J mol}^{-1} \text{ K}^{-1}$, $\log k_{298} = 0,9 \pm 0,3$). Density functional theory (DFT) calculations have been carried out to reveal the effect of protonation and the role of solvent.

The solid structures of $\text{In}(\text{edta})^-$ and $\text{Tl}(\text{edta})^-$ complexes are different. In(III) is seven-coordinated in a trigonal prismatic fashion by a hexadentate edta and one water molecule in solid, while in the newly prepared $\text{Tl}^{\text{I}}\text{Tl}^{\text{III}}(\text{edta})\cdot 2\text{H}_2\text{O}$ the $\text{Tl}(\text{edta})^-$ anion has **distorted octahedral structure**. However the structures and the ^1H and ^{13}C NMR spectra of these complexes are very similar in solution, the acetate arms are equivalents, there is no fluxionality observed at these actual NMR time scales.

$M(\text{edta})(\text{OH})^{2-}$ complexes ($M = \text{Ga}, \text{In}, \text{Tl}$) have also been detected, pK values in D_2O are -6.08 ± 0.06 and -9.17 ± 0.07 and 6.63 ± 0.05 , respectively. (Paper 4, manuscripts 6 and 7)

3.3. The structures of some **(CN)₅Pt–Tl(APC) complexes** in aqueous solutions have been studied and determined by multinuclear NMR spectroscopy. The $[(\text{CN})_5\text{Pt–Tl}_{(s)}]^0$ complex is soluble in 1 eq. APC ligand solution **without decomposition the Pt–Tl metal-metal bond in case of APC = nta and mimda**. The **(CN)₅Pt–Tl(edta)⁴⁻ partially decomposes** to $[\text{Pt}(\text{CN})_4]^{2-}$ and $\text{Tl}(\text{edta})\text{CN}^{2-}$. However, the complex having metal-metal bond can proceed from $[\text{Pt}(\text{CN})_4]^{2-}$ and $\text{Tl}(\text{edta})\text{CN}^{2-}$ also, therefore $(\text{CN})_5\text{Pt–Tl}(\text{edta})^{4-}$ is an intermediate of a real equilibrium. We have presented here the constant of equilibria, formation and decomposition kinetics and mechanism of the $(\text{CN})_5\text{Pt–Tl}(\text{edta})^{4-}$. Compound **(CN)₅Pt–Tl(нта)³⁻** has been prepared in solid and the structure determined by single-crystal X-Ray diffraction. Both metal centers have slightly distorted octahedral geometry, five C-bonded cyanide and the Tl atom coordinated to the Pt atom, while the Tl is surrounded by the Pt, three carboxylate O atoms and the N donor of nta together with a water molecule. The structure is fluxional in solution. The structures of $(\text{CN})_5\text{Pt–Tl}(\text{edta})^{4-}$ complex and some intermediates of decomposition with short lifetime have been optimised by DFT calculation . (Manuscript 5)

3.4. Well defined adducts **K₂PtHg(CN)₆·2H₂O (1)**, **Na₂PdHg(CN)₆·2H₂O (2)** and **K₂NiHg(CN)₆·2H₂O (3)** can be prepared and characterized in the solid phase by means of single-crystal X-ray diffraction. The structure of **K₂PtHg(CN)₆·2H₂O (1) consists of one-dimensional –Pt–Hg–Pt–Hg– wires**. No CN^- bridges were observed between the heterometallic centers. The wire is strictly linear and the Pt(II) and Hg(II) centers alternate; $d_{\text{Hg–Pt}} = 3.460 \text{ \AA}$, is relatively short. Time resolved luminescence spectra indicate that $\text{Hg}(\text{CN})_2$ units

incorporated into the structure act as electron traps and shorten the lifetimes of both the short-lived and the longer-lived excited states in **(1)** compared to $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$. The quenching mechanism might be an electron transfer instead of an energy transfer process.

The other adducts, **$\text{Na}_2\text{PdHg}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ (2) and $\text{K}_2\text{NiHg}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ (3)** do not show similarity with the structure of **(1)**. The structures can be considered as **double salts**, the lack of hetero-metallophilic interaction between both remote Hg(II) and Pd(II) atoms, $d_{\text{Hg-Pd}} = 4.92 \text{ \AA}$, and Hg(II) and Ni(II) atoms, $d_{\text{Hg-Ni}} = 4.61 \text{ \AA}$, seems to be obvious. Electron binding energy values of the metallic centers measured by XPS show that no electron transfer between the metal ions occurs in the three adducts. An interaction between $\text{Hg}(\text{CN})_2$ and square planar $[\text{M}^{\text{II}}(\text{CN})_4]^{2-}$ transition metal cyanides (M = Pt, Pd or Ni, with d^8 electron shell) does not result in a metal-metal bond formation in solution in contrast to the isoelectronic $[\text{Pt}^{\text{II}}(\text{CN})_4]^{2-} - \text{Tl}^{\text{III}}(\text{CN})_n^{+3-n}$ system, revealing a strong and not supported Pt-Tl bond. (Paper 2)

4. PUBLICATIONS

7. M. Purgel, **R. Józszai**, I. Pápai, L. Zékány, I. Bányai and I. Tóth:
 ^1H , ^{13}C NMR and DFT Study of the Al(III)-ethylenediamine-tetraacetate Complex in Solution. Mechanism of the Proton and/or Water Assisted Fluxionality.
Manuscript in preparation

6. **R. Józszai**, A. C. Bényei, L. Zékány I. Pápai and I. Tóth:
Multinuclear NMR and DFT Studies of the Structure for Tl(III)-ethylenediamine-tetraacetate Complex in Solution. X-ray Structure of $\text{Tl}^{\text{I}}[\text{Tl}^{\text{III}}(\text{edta})]\cdot 2\text{H}_2\text{O}$.
Manuscript in preparation

5. **R. Józszai**, A. Fischer, M. Maliarik, J. Glaser and I. Tóth:
Modification of the metal-metal bonded cluster, $(\text{CN})_5\text{Pt-Tl}(\text{CN})_n$: the reaction of the Tl-center with aminopolycarboxylate ligands.
Manuscript in preparation

4. **Róbert Józszai**, Mihály Purgel, Imre Pápai, Hisanobu Wakita and Imre Tóth
Multinuclear NMR and DFT Studies of the Structure and Fluxionality for M^{III} -ethylenediamine-tetraacetate Complexes ($\text{M}(\text{edta})^-$, $\text{M} = \text{Al, Ga and In}$) in Solution.
J. of Molecular Liquids, **2006**, in press

3. **Róbert Józszai**, Imola Kerekes, Igarashi Satoshi, Kiyoshi Sawada, László Zékány and Imre Tóth
Equilibrium and Structure of the Al(III)-Ethylenediamine-N,N'-bis 3-hydroxy-2-propionate (EDBHP) Complex. A Multi-method Study by Potentiometry, NMR, ESI MS and X-ray Diffraction.
Dalton Trans. **2006**, DOI:10.1039/b517192

2. **Róbert Józszai**, Imre Beszeda, Attila C. Bényei, Andreas Fisher, Margit Kovács, Mikhail Maliarik, Péter Nagy, Andrey Shchukarev and Imre Tóth
Metal-metal bond or isolated metal centers? Reaction of $\text{Hg}(\text{CN})_2$ with square planar transition metal cyanides.
Inorg. Chem., **2005**, *44*, 9643-9651.

1. Péter Nagy, **Róbert Józszai**, István Fábián, Imre Tóth and Julius Glaser
The Decomposition and Formation of the Platinum-Thallium Bond in the $[(\text{CN})_5\text{Pt-Tl}(\text{edta})]^{4-}$ Complex. Kinetics and Mechanism.
Juornal of Molecular Liquids, **2005**, *118*, 195-207.

POSTERS AND LECTURES

17. **R. Józai**, I. Bányai, A. Bényei, M. Purgel, I. Pápai, H. Wakita and I. Tóth
Multinuclear NMR Study of the Structure and Fluxionality of M^{III} -
ethylenediamine-tetraacetate ($M(edta)$, $M=Al, Ga, In$ and Tl) Complexes in
solution.
29 ICSC, Szlovénia, Portoroz, **2005**, Book of Abstracts, AP18, p. 81.
16. **R. Józai**, I. Bányai, A. Bényei, M. Purgel, I. Pápai, H. Wakita and I. Tóth
Multinuclear NMR Study of the Structure and Fluxionality of M^{III} -
ethylenediamine-tetraacetate ($M(edta)$, $M=Al, Ga, In$ and Tl) Complexes in
solution.
*MPG/MOEL-Symposium Magnetic Resonance in Physics, Chemistry, Biology and
Medicine*, Berlin-Dresden, 22.-25. May **2005**, Book of Abstracts, P 4.
15. **I. Tóth**, **R. Józai**, P. Nagy, I. Fábán, M. Maliarik and J. Glaser
Naked $Tl-Pt$ Bonded Small Cyano Clusters: New Results.
*Euresco Conference, Inorganic Chemistry, EuroConference on New Theoretical
and Spectroscopical Approaches to Inorganic Chemistry*, San Feliude Guixols
2004, Book of Abstracts, 75, p. 86.
14. **R. Józai**, I. Kerekes, I. Satoshi, K. Sawada and I. Tóth
Equilibrium and Structure of $Al(EDDHP)$ Complex.
*Euresco Conference, Inorganic Chemistry, EuroConference on New Theoretical
and Spectroscopical Approaches to Inorganic Chemistry*, **2004**, Book of Abstracts,
37, p. 56.
13. **Józai Róbert**, Kerekes Imola, Igarashi Satoshi, Sawada Kiyoshi és Tóth Imre
Az $Al(EDDHP)$ komplex oldategyensúlyi és szerkezeti vizsgálata.
XXXIX. Komplexkémiai Kollokvium, Agárd-Gárdony, **2004**, Book of Abstracts p.
18.
12. **P. Nagy**, **R. Józai**, I. Fábán, I. Tóth and J. Glaser
Kinetics and mechanism of formation and decomposition of $(CN)_5PtTl(edta)^{4-}$.
Inorganic Reaction Mechanism Meeting, Athens, Greece, **2004**, Book of Abstracts,
p. P37.
11. **P. Nagy**, **R. Józai**, I. Fábán, and I. Tóth
Formation kinetic studies on the $(CN)_5PtTl(edta)^{4-}$ complex.
Inorganic Mechanism Discussion Group, Newcastle, England, **2003**.
10. **R. Józai** and I. Tóth
Measuring pH in the NMR tube: combination pH-potentiometry with multinuclear
NMR.

Ifjú analitikusok napja, Budapest, November 25, 2003.

9. P. Nagy, **R. Józai**, I. Fábrián and I. Tóth
Kinetics and mechanism of formation and decomposition of $(\text{CN})_5\text{Pt-Tl}(\text{edta})^{4-}$.
28th International Conference on Solution Chemistry, Debrecen, August 23-28, 2003, Book of Abstracts, p. 52.

8. T. Yokoyama, I. Tóth, **R. Józai** and H. Wakita
 ^{13}C and ^{27}Al study on the aluminium complexes with fulvic acid and related ligands in acid solution.
28th International Conference on Solution Chemistry, Debrecen, August 23-28, 2003.

7. **R. Józai**, I. Kerekes, I. Satoshi, K. Sawada and I. Tóth
Equilibrium and Structure of $\text{Al}(\text{EDDHP})$ Complex.
28th International Conference on Solution Chemistry, Debrecen, August 23-28, 2003, Book of Abstracts, p. 145.

6. **Józai R.**, P. Nagy, I. Tóth, M. Malariik and J. Glaser
Structural characterisation of direct Pt-Tl bonded complexes.
4th Central European NMR symposium and 4th Central European Bruker NMR users meeting, Budapest, September 2-3, 2002, Book of Abstracts, p. 15.

5. I. Tóth, **R. Józai**, P. Nagy, I. Fábrián, M. Malariik, J. Glaser
Naked Pt-Tl bonded small cyano clusters: results and questions marks.
Inorganic Chemistry EuroConference on the Inorganic Side of Molecular Architecture, San Feliude Guixols, Spanyolország, 2002.

4. **R. Józai**, P. Nagy, I. Fábrián, and I. Tóth
Kinetic studies of formation and decomposition of $(\text{CN})_5\text{Pt-Tl}(\text{edta})^{4-}$.
XXXVII. Komplexkémiái Kollokvium, Mátraháza, May 29-31, 2002, Book of Abstracts, p. 15.

3. **R. Józai**, I. Tóth, M. Malariik and J. Glaser
Modification of the metal-metal bonded clusters, $(\text{CN})_5\text{Pt-Tl}(\text{CN})_n$: the reaction of the Tl-center with aminopolycarboxylate ligands.
Erdélyi Magyar Műszaki Tudományos Társaság, VII. Chemistry Conference, Félix-fürdő (Románia), November 16-18, 2001, Book of Abstracts, p. 59-62.

2. **R. Józai**, I. Tóth, M. Malariik and J. Glaser
Modification of the metal-metal bonded clusters, $(\text{CN})_5\text{Pt-Tl}(\text{CN})_n$: the reaction of the Tl-center with aminopolycarboxylate ligands.
10th Science Meeting of MTA Szabolcs-Szatmár-Bereg County, Nyíregyháza, September 29, 2001, Book of Abstracts, p. 39.

1. **R. Józai**, I. Tóth , M. Malariik and J. Glaser
Reaction of the metal-metal bonded clusters, $(\text{CN})_5\text{Pt-Tl}(\text{CN})_n$ with aminopolycarboxylate ligands.
XXXVI. Komplexkémiai Kollokvium, Pécs, May 23-25, **2001**, Book of Abstracts, p. 9.