

**Summary of PhD thesis**

**Robust thallium(III) complexes with inorganic and organic  
multidentate ligands**

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## I. Introduction and objectives

Called the “forgotten element” of the periodic table by some, the research of thallium chemistry research cannot be described as either widespread or mainstream. Indeed to most people, both outside and within the scientific community, the most widely known properties of thallium are its toxicity and its use as poison for rodents and sometimes humans. Ongoing inorganic thallium chemistry is mostly confined to its redox reactions, high-temperature Tl-containing superconductors, metal-metal bonds and its coordination chemistry. Thallium is used in a variety of fields (optical industry, electronics, in good quality bearings as alloys) and less so in medicine: intravenous injections of  $^{201}\text{Tl}$  for myocardial imaging.

Tl(III) is classified as a „soft” metal ion, in contrast to other elements of the group, which are classified as „hard” ions. The „softness” of Tl(III) is shown in its strong interactions with „soft” donor ligands such as sulphur or larger halides. As such, Tl(III) forms strong halido-complexes. These species are more stable in aqueous solution than analogous complexes of other group 13 elements and are among the most stable known. It also forms stable cyanide complexes, which are in fact the most stable monodentate–Tl(III) complexes.

One of the more interesting aspects of the ion is its propensity to form extremely stable complexes with multidentate ligands. These will most often stabilize the cation against both hydrolysis and reduction, as exemplified in the  $[\text{Tl}(\text{edta})]^-$  complex, which is the second most stable metal–edta species known, being trumped only by  $[\text{Co}^{\text{III}}(\text{edta})]^-$ .

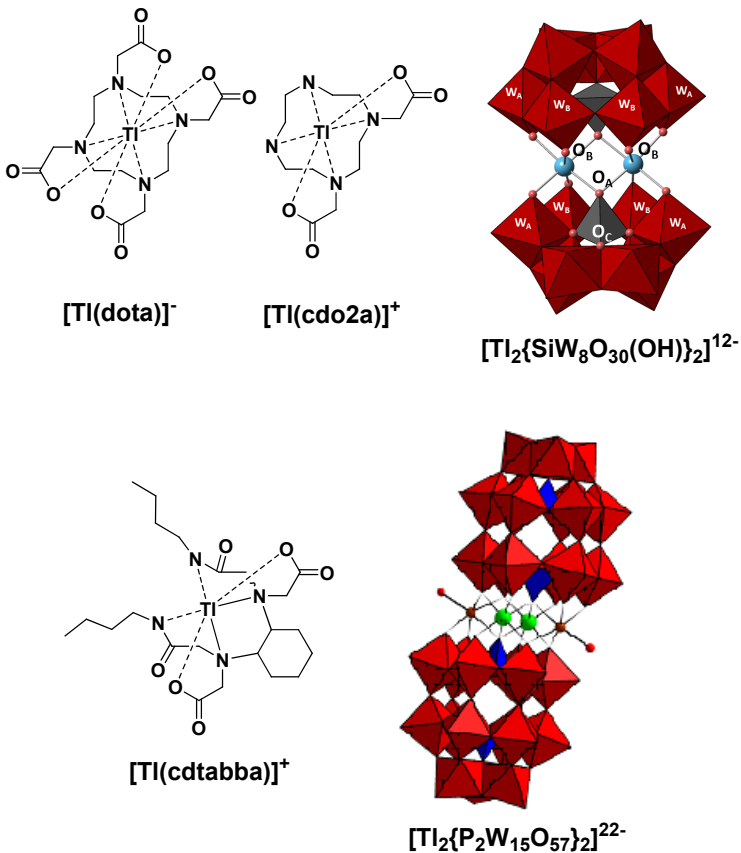
The metal ion in  $[\text{Tl}(\text{edta})]^-$  also possesses one free coordination site, enabling it to form ternary  $[\text{Tl}(\text{edta})\text{X}]^{2-}$  complexes with monodentate ligands readily. These mixed-ligand complexes, formed mainly with halides and

pseudohalides, are also quite stable. The combination of high stability and anion binding has sparked interest in the usage of Tl(III) complexes as transports for imaging radionuclides, such as  $^{131}\text{I}$ .  $[\text{Tl}(\text{edta})\text{X}]^{2-}$ -like compounds however, dissociate far too rapidly to be of real use in medicine. Such kinetic lability is usually overcome by the use of macrocyclic ligands and/or modification of some, or all donor groups on existing ligands.

Cyclic polyamino–polycarboxylate ligands are naturally expected to yield even greater stability and improved inertness to their respective metal complexes. Data on the chemical equilibria and structure of such Tl(III)–complexes is even more scarce however, which has made the expansion of this knowledge one objective of this work.

Another goal was to gain insight to the chemistry and structure of newly synthesized thallium–containing polyoxometallates (POMs). The area of Tl(III)-containing POMs is virtually unexplored and only little work has been performed on thallium tungstates. These are derivatives of vacant polytungstate structures. Such lacunary POMs are usually prepared by hydrolytically removing a controlled number of  $\text{MO}_x$  groups and are markedly more reactive than their parent compounds. They are in essence, inorganic multidentate ligands and as such, are also expected to provide Tl(III)–complexes with heightened stability and inertness.

## II. Studied compounds



**Figure 1.** Structure of the studied compounds

## III. Experimental methods

**pH measurements.** pH values were measured by a Metrohm 6.0234.100 combined glass electrode connected to a Delta Ohm HD 8705 pH-meter. Measurements were performed at 25 ( $\pm 0.1$ ) °C, in 1M NaClO<sub>4</sub>. The bridge

electrolyte (3M KCl) in the electrode was replaced with 1M NaCl to avoid KClO<sub>4</sub> precipitation in the membrane. Aside from regular pH-measurements, potentiometry was used to determine the protonation constants of the organic ligands and formation constants of [Tl(cdo2a)OH] and [Tl(cdo2a)OH<sub>2</sub>]<sup>-</sup>.

**pI measurements** were used for the potentiometric investigation of iodide-binding to [Tl(cdo2a)]<sup>+</sup> and [Tl(cdtabba)]<sup>+</sup> using a Metrohm 6.0502.160 iodide-selective electrode with an Ag/AgCl electrode as reference. Measurements were performed at 25 (±0.1) °C, in 1M NaClO<sub>4</sub>.

**Spectrophotometry** was used to investigate the dissociation kinetics of [Tl(cdo2a)]<sup>+</sup> and [Tl(dota)]<sup>-</sup>. UV-VIS spectra were recorded in quartz cuvettes with 1.0 mm path length with a Varian Cary 1E UV-Visible Spectrophotometer at 25 °C in the wavelength range 350-200 nm. Short-term dissociation kinetics were followed by repeated recordings of spectra, with delay times of 1 hour. The UV-light was cut off from the sample during the delays to avoid photochemical decomposition. Long-term kinetics were followed by separate recordings, with delay times of 1 day or 1 week.

**NMR measurements.** <sup>1</sup>H and <sup>13</sup>C spectra were recorded with a Bruker AM 400 spectrometer, at 400.1 MHz and 100.6 MHz, respectively. Thallium spectra were obtained at 8.46 Tesla on a Bruker AM 360 spectrometer by inserting a 500 MHz BB probe and tuning the x-channel to the frequencies of <sup>205</sup>Tl (207.74 MHz) or <sup>203</sup>Tl (205.72 MHz), and at 5.87 Tesla using a 400 MHz probe in a Bruker Avance 250 spectrometer (ELTE NMR Laboratory, Budapest) at the respective frequencies for <sup>205</sup>Tl (144.28 MHz) and <sup>203</sup>Tl (142.88 MHz). Line-shape analysis was carried out with a home-made program written in MatLab. <sup>1</sup>H and <sup>13</sup>C NMR, <sup>1</sup>H-<sup>1</sup>H COSY and <sup>1</sup>H-<sup>13</sup>C HSQC were used to investigate the structure and

fluxional behaviour of  $[\text{Tl}(\text{dota})]^-$ ,<sup>205</sup> and <sup>203</sup>Tl NMR were used to investigate mixed complex formation of  $[\text{Tl}(\text{cdo}2\text{a})]^+$  and  $[\text{Tl}(\text{dota})]^-$  with halides and cyanide and the stability and structure of  $[\text{Tl}_2\{B\text{-}\beta\text{-SiW}_8\text{O}_{30}(\text{OH})\}_2]^{12-}$  and  $[\text{Tl}_2\{\text{P}_2\text{W}_{15}\text{O}_{57}\}_2]^{22-}$ . Probe temperatures were kept at 25 ( $\pm 0.1$ ) °C in most cases and was varied between  $-1$  and 81 °C when investigating the internal conversions of  $[\text{Tl}(\text{dota})]^-$ .

**Single crystal X-ray diffraction crystallography** was used to obtain the solid structure of  $[\text{Tl}(\text{dota})]^-$  and  $[\text{Tl}_2\{B\text{-}\beta\text{-SiW}_8\text{O}_{30}(\text{OH})\}_2]^{12-}$ . In case of  $\{\text{C}(\text{NH}_2)_3\}[\text{Tl}(\text{dota})]\cdot\text{H}_2\text{O}$ , diffraction intensity data collection was carried out at 293(2) K on a Bruker-Nonius MACH3 diffractometer equipped with a point detector using graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å).  $(\text{NH}_4)_5\text{K}_7[\text{Tl}_2\{B\text{-}\beta\text{-SiW}_8\text{O}_{30}(\text{OH})\}_2]\cdot 19\text{H}_2\text{O}$  was mounted onto a Hampton cryoloop in light oil for data collection at 100 K. The data were collected on a Bruker Kappa X8 APEX 2 CCD single-crystal diffractometer equipped with a sealed molybdenum tube and a graphite monochromator ( $\lambda = 0.71073$  Å). Both structures were solved with the direct methods and refined by the full-matrix least-squares method on  $F^2$ .

**DFT calculations.** The arm rotation and ring inversion processes of  $[\text{Tl}(\text{dota})]^-$  were investigated by means of the synchronous transit-guided quasi-Newton method at the B3LYP/CRENBL/6-31+G(d,p) level. The nature of the saddle points (one imaginary frequency) was characterized by frequency analysis. The free energy barriers calculated include non-potential energy contributions obtained by frequency analysis.

The NMR shielding tensors of the  $[\text{Tl}(\text{dota})]^-$  system were calculated in aqueous solution using the B3LYP functional and the GIAO method. In these calculations the more extended 6-311G+(d,p) basis set was used for the ligand atoms. For <sup>13</sup>C-

NMR chemical shift calculation purposes the NMR shielding tensors of TMS were calculated at the same level. Throughout this work solvent effects were included by using the polarizable continuum model (PCM). Calculations were also performed with MS Excel, PSEQUAD and OriginPro.



## IV. New scientific results

### IV.1. Structural properties of $[\text{Tl}(\text{dota})]^-$ have been explored both in solid phase and solution. The complex possesses a highly compact structure, devoid of additional metal-coordinated small molecules.

In solid state, the  $\text{Tl}^{3+}$  ion is directly coordinated to the eight donor atoms of the ligand, with the metal coordination environment being best described as twisted square antiprismatic (TSAP); the coordination of the ligand to the metal ion introduces two sources of stereoisomerism, one associated to the conformation of the cyclen moiety  $[(\delta\delta\delta\delta)$  or  $(\lambda\lambda\lambda\lambda)]$ , and another related to the layout of the four acetate pendant arms [represented as  $\Delta$  or  $\Lambda$ ]. Inspection of the structure shows that crystals contain the  $\Lambda(\lambda\lambda\lambda\lambda)/\Delta(\delta\delta\delta\delta)$  enantiomeric pair, the two enantiomers being centro-symmetrically related in accordance with the centro-symmetric character of the space group P-1. The “soft” nature of  $\text{Tl}^{3+}$  (and  $\text{Bi}^{3+}$ ) according to the Pearson classification provokes a strengthening of the coordination bonds with the softer N donor atoms, which results in a deeper penetration of the metal ion into the macrocyclic cavity and the preclusion coordination of further water molecules or small ions to the metal center.

The (proton coupled)  $^{205}\text{Tl}$ -NMR spectrum of  $[\text{Tl}(\text{dota})]^-$  in solution shows a single signal at  $\delta = 2218$  ppm with a chemical shift very similar to that measured earlier for  $[\text{Tl}(\text{edta})]^-$  ( $\delta = 2301$  ppm). The absence of a signal due to  $\text{Tl}^{3+}_{\text{aq}}$  at  $\delta = 2039$  ppm confirms the full complexation of the metal ion by the ligand.  $[\text{Tl}(\text{dota})]^-$  is present in solution as a mixture of two TSAP isomers  $\Lambda(\lambda\lambda\lambda\lambda)$  and  $\Delta(\delta\delta\delta\delta)$ , while no significant populations of the SAP' isomers could be detected by NMR spectroscopy.

**IV.2. The acid–base properties and affinities towards mixed–complex formation were investigated for  $[\text{Tl}(\text{cdo2a})]^+$ ,  $[\text{Tl}(\text{cdtabba})]^+$  and  $[\text{Tl}(\text{dota})]^-$ . The coordinative saturation around the metal center and overall compactness in  $[\text{Tl}(\text{dota})]^-$  makes further coordination of small anions unfavourable.  $[\text{Tl}(\text{cdo2a})]^+$  and  $[\text{Tl}(\text{cdtabba})]^+$  were found to form a relatively stable mixed–complex with iodide ions.**

The complexes are highly resistant towards dissociation via proton– or  $\text{OH}^-$ –assisted pathways.  $[\text{Tl}(\text{dota})]^-$  does not deprotonate in the pH–range 4–11, as there is no room for a Tl–coordinated water molecule in the complex, however a protonation constant of  $\text{pK}_{[\text{Tl}(\text{dota})]}^{\text{H}} = 1.4 \pm 0.1$  was obtained from  $^{205}\text{Tl}$ -NMR. This process most likely involves the protonation of one of the carboxylate arms. It is likely that  $[\text{Tl}(\text{dota})]^-$  may be stored on any measurable pH indefinitely. Conversely,  $[\text{Tl}(\text{cdo2a})]^+$  and  $[\text{Tl}(\text{cdtabba})]^+$  do have coordinated water molecules – owing to fewer donor donor atoms and favourable structure of the ligands – and can be deprotonated twice ( $\text{lgK}_{[\text{Tl}(\text{cdo2a})]}^{\text{OH}} = -7.37 \pm 0.008$ ,  $\text{lgK}_{[\text{Tl}(\text{cdo2aOH})]}^{\text{OH}} = -11.10 \pm 0.009$ ,  $\text{lgK}_{[\text{Tl}(\text{cdtabba})]}^{\text{OH}} = -6.04 \pm 0.003$  és  $\text{lgK}_{[\text{Tl}(\text{cdtabbaOH})]}^{\text{OH}} = -8.80 \pm 0.004$ ). Protonation at low pH has not been measured, although these complexes also stay intact in the pH–range 0–12 for months.

$[\text{Tl}(\text{dota})]^-$  does not form mixed–complexes generally due to the metal being virtually completely wrapped by the ligand donor groups. Only the formation of a faint mixed  $[\text{Tl}(\text{dota})(\text{CN})]^{2-}$  complex could be detected, possessing a  $^{205}\text{Tl}$ -NMR signal at  $\delta = 2463$  ppm, with  $K_{\text{mix}} = 6.0 \pm 0.8$ . This is 8 orders of magnitude lower than the  $\text{lgK}_{\text{mix}} = 8.7$  obtained for  $[\text{Tl}(\text{edta})(\text{CN})]^{2-}$ . Both  $[\text{Tl}(\text{cdo2a})]^+$  and  $[\text{Tl}(\text{cdtabba})]^+$  were shown to readily form halido–mixed ligand complexes by potentiometric titrations and  $^{205}\text{Tl}$  NMR. Formation constants of  $\text{lgK}_{[\text{Tl}(\text{cdo2a})]}^{\text{I}} = 4.1 \pm 0.1$  and  $\text{lgK}_{[\text{Tl}(\text{cdtabba})]}^{\text{I}} = 5.73 \pm 0.79$  were obtained from

potentiometry with an iodide-selective electrode titrations in the pH-range 3–4 (avoiding the interference of OH<sup>-</sup>). In the case of [Tl(cdo2a)I], the obtained value is also supported by <sup>205</sup>Tl NMR

**IV.3. Dissociation kinetics of [Tl(cdo2a)]<sup>+</sup> and [Tl(dota)]<sup>-</sup> were investigated. Both complexes were found to be highly stable and inert against dissociation, requiring large excesses of competing agents (Br<sup>-</sup> and H<sup>+</sup>) for the dislocation of Tl(III) to occur, even so, quite slowly.**

Several attempts were made to determine the stability of both [Tl(cdo2a)]<sup>+</sup> and [Tl(dota)]<sup>-</sup> using the double competition method previously described for [Tl(edta)]<sup>-</sup>, using large (in some cases, several thousand-fold) excesses of both Br<sup>-</sup> and H<sup>+</sup> in batch samples, followed via UV-spectrophotometry. True equilibration could not however be reached in case of either complex, as some unknown side-reaction takes place which interferes with the evaluation of UV-spectra from then on.

Insight into the dissociation of [Tl(dota)]<sup>-</sup> was however obtained, using the initial rate method. The rate law is given in the following form:

$$-d[\text{Tl(dota)}]_t/dt = k_{\text{obs}}[\text{HTl(dota)}]_t \quad (1)$$

$$k_{\text{obs}} = k_0 + k_1[\text{H}^+] + k_2[\text{H}^+]^2 \quad (2)$$

The data shows quadratic dependence of  $k_{\text{obs}}$  on acidity, with no detectable spontaneous dissociation. Curve fitting gives  $k_0 = 0$  (value fixed, as trials returned a small negative value with large error),  $k_1 = (9 \pm 7) \times 10^{-7} \text{ s}^{-1} \text{ M}^{-1}$  and  $k_2 = (5 \pm 0.8) \times 10^{-6} \text{ s}^{-1} \text{ M}^{-2}$  values. The  $k_1$  value also has a large uncertainty, and may

as well be a calculation artifact. This kind of rate law is however in accordance with those found in the related literature of dota-complexes, i.e. the dissociation is a dominantly proton-assisted process. Using the  $k_{\text{obs}} = k_1[\text{H}^+] + k_2[\text{H}^+]^2$  rate equation, the half-life of the complex at different pH values can be calculated. Half-life of  $[\text{Tl}(\text{dota})]^-$  is 32 h in 1 M  $\text{HClO}_4$  and approximated to  $5 \cdot 10^9$  h (more than half million years) at pH = 7.4. The latter value indicates that the dissociation of  $[\text{Tl}(\text{dota})]^-$  at the physiological pH of blood is negligible.  $[\text{Tl}(\text{cdo}2\text{a})]^+$  behaves similarly, with faster dissociation and lower acid concentrations needed to initiate the process (4 hours in 1 M  $\text{HClO}_4$  and 786 hours at pH = 7.4).

**IV.4. Dynamics of the isomer–interconversion (enantiomerization) observed in  $[\text{Tl}(\text{dota})]^-$  were elucidated by line shape analysis. The shape change in  $^{13}\text{C}$  NMR is attributed to the chemical exchange comprised of inversion of the macrocyclic ring  $[(\lambda\lambda\lambda\lambda) \leftrightarrow (\delta\delta\delta\delta)]$  and consecutive rotation of the acetate arms  $[\Lambda \leftrightarrow \Delta]$ .**

Fortunately, the complete transition from slow – to fast exchange can be observed at conventional temperatures and quantitative band-shape analysis of the  $\Lambda(\lambda\lambda\lambda\lambda) \leftrightarrow \Delta(\delta\delta\delta\delta)$  ring-inversion process provides the exchange rates  $k_{\text{exch}}$  at every temperature, which were subsequently used to obtain activation parameters for the process. The obtained values are in good agreement with those found by DFT.

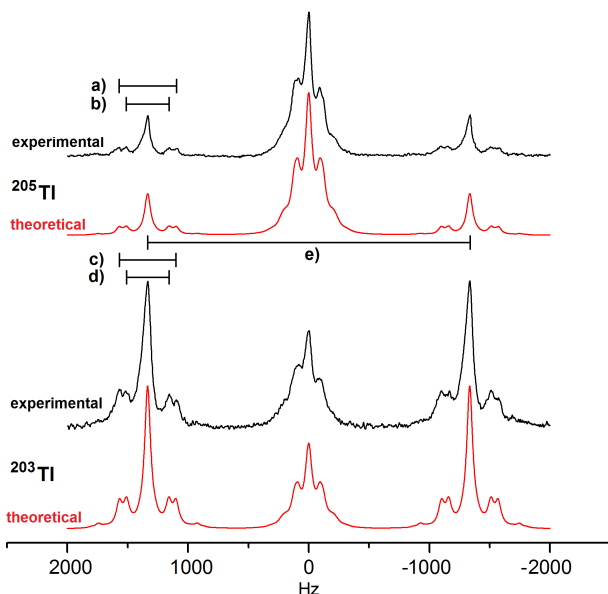
**IV.5. The ternary fluorido complex of [Al(nota)] (somewhat similar to [Tl(dota)]<sup>-</sup> in structure and robustness) was investigated. [Al(nota)(F)]<sup>-</sup> could only be detected with <sup>19</sup>F NMR in a competition reaction between Al(III), nota and F<sup>-</sup> in a metastable system.**

Contrary to literature, the formation of the ternary [Al(nota)(F)]<sup>-</sup> via direct reaction of [Al(nota)] and F<sup>-</sup> cannot be detected either via potentiometry or <sup>19</sup>F NMR spectroscopy. The desired product can only be found in detectable amounts in solutions containing equimolar amounts of nota, Al(III) and F<sup>-</sup> after heating, although no equilibrium data could be compiled. Yield of the ternary complex can be raised to almost 100% using 50% ethanol as solvent. What occurs is likely a multi-step competition reaction between the various Al(III)–fluorido species and nota through the intermediate [Al(nota)F], as increased heating times decrease yield and provide the parent complex [Al(nota)].

**IV.6. Solution structure of two thallium(III)–containing POMs were investigated. The solid structure is fully retained in solution as evidenced by <sup>205</sup> and <sup>203</sup> Tl NMR spectra. We have interpreted the fine structure of the spectra and simulated the complex spin systems. We have also determined the conditional stability constant for the complex [Tl<sub>2</sub>{*B*-β-SiW<sub>8</sub>O<sub>30</sub>(OH)}<sub>2</sub>]<sup>12-</sup>.**

In solid (NH<sub>4</sub>)<sub>5</sub>K<sub>7</sub>[Tl<sub>2</sub>{*B*-β-SiW<sub>8</sub>O<sub>30</sub>(OH)}<sub>2</sub>]·19H<sub>2</sub>O the [Tl<sub>2</sub>{*B*-β-SiW<sub>8</sub>O<sub>30</sub>(OH)}<sub>2</sub>]<sup>12-</sup> architecture presents a polyanion with idealized C<sub>2h</sub> symmetry, which consists of two thallium(III) centers and two {*B*-β-SiW<sub>8</sub>O<sub>31</sub>} POM units. The two thallium(III) centers are both six-coordinated, and each thallium ion is coordinated to two {*B*-β-SiW<sub>8</sub>O<sub>31</sub>} lacunary POM fragments via four terminal O atoms of the two complete tungsten-oxo triads and two terminal O atoms of two

{SiO<sub>4</sub>} hetero groups. This structure is fully retained in solution and contains two thallium centers within scalar coupling distance, as evidenced by <sup>205</sup>Tl and <sup>203</sup>Tl NMR spectra. Both spectra appear as pseudo-triplets attributed to the spin-spin coupling between two sterically identical Tl-atoms. Further fine structure can be observed due to spin-spin coupling with <sup>183</sup>W atoms (14.3%). The two different values for <sup>2</sup>J(<sup>203</sup>Tl-<sup>183</sup>W) are ca. 470 and 350 Hz, respectively, and the corresponding values for <sup>2</sup>J(<sup>205</sup>Tl-<sup>183</sup>W) are ca 1% larger. These values can be rationalized by coupling to two structurally inequivalent types of tungsten being two bonds away from the thallium centers.



**Figure 2.** Experimental (black) and theoretically simulated (red) 144.26 MHz <sup>205</sup>Tl (top) and 142.86 MHz <sup>203</sup>Tl NMR spectra of compound 1, ~6 mM in 0.04 M acetic acid/sodium acetate buffer, pH = 4.1.

We have also simulated the Tl NMR spectra considering the symmetry of  $[\text{Ti}_2\{B\text{-}\beta\text{-SiW}_8\text{O}_{30}(\text{OH})\}_2]^{12-}$ , the relative positions of the Tl and W atoms, the natural abundance of the NMR-active nuclei and the spin-spin coupling constants measured experimentally. Experimentally obtained NMR spectra are a superposition of several constituent spectra with different combinations of NMR-active nuclei. In our simulated model only the Tl-O-Tl and Tl-O- $^{183}\text{W}$  couplings were considered, leading to 54 different possible spin systems. The easily detectable shape difference between the central and the satellite peaks can be attributed to the fact that the  $^{183}\text{W}$  atoms are coupled to homonuclear-coupled Tl atoms ( $A_2$  spin system), resulting in magnetic nonequivalence of the chemically equivalent two  $^{205}\text{Tl}$  or  $^{203}\text{Tl}$  atoms, creating an  $AA'X$  spin system. In such a spin system the Tl-W splitting is just half of that observed for the satellite signals. The theoretical spectra shown in the figure have been simulated as the superposition of 60 Hz wide Lorentzians with the calculated positions and relative integrated intensities of peaks.

The same is visible in  $[\text{Ti}_2\{\text{P}_2\text{W}_{15}\text{O}_{57}\}_2]^{22-}$ , although there is less distance between the central and satellite peaks and the two coupled  $^{31}\text{P}$  nuclei (100% natural abundance) also provide added multiplicity to all thallium signals. The compound clearly retains its structure in solution and the obtained peak groups in  $^{203}$  and  $^{205}\text{Tl}$  NMR can both be nicely reconstructed as the sum of an adequate “amount” of pure central and satellite intensities. The spectra also contain a minor signal group which also seems to contain two Tl(III) nuclei, but is somewhat different in both chemical shift and peak structure.

NMR–titration of  $[\text{Ti}_2\{B\text{-}\beta\text{-SiW}_8\text{O}_{30}(\text{OH})\}_2]^{12-}$  with acetate ions as a competing agent for thallium has also yielded some insight into its stability. No visible reaction took place with large acetate–excess, even after several days.

Considering the substance as an  $M_2L_2$  complex comprised of 2 thallium ions and 2  $\{B\text{-}\beta\text{-SiW}_8\text{O}_{31}\}$  units an estimated minimum stability of  $\lg K > 40$  was calculated, although polytungstates are known to often possess extremely slow kinetics. From this it can be extrapolated that –barring any additional effect– the compound will only undergo dissociation due to dilution in the sub–nanomolar range. It is worth noting that  $[\text{Tl}_2\{B\text{-}\beta\text{-SiW}_8\text{O}_{30}(\text{OH})\}_2]^{12-}$  is shown to decay into a mixture of polytungstates, each containing only one Tl(III) by Tl NMR, however this only occurs after several months and dissociated thallium –either as oxide or acetate– complex– remains absent.





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Subject: PhD Publikációs Lista

Candidate: Tamás Fodor  
Neptun ID: RW7RL1  
Doctoral School: Doctoral School of Chemistry

### List of publications related to the dissertation

#### Foreign language scientific articles in international journals (2)

1. Farkas, E., **Fodor, T.**, Kálmán, F. K., Tircsó, G., Tóth, I.: Equilibrium and dissociation kinetics of the [Al(NOTA)] complex (NOTA=1,4,7-triazacyclononane-1,4,7-triacetate). *React. Kinet. Mech. Catal.* **116** (1), 19-33, 2015. ISSN: 1878-5190.  
DOI: <http://dx.doi.org/10.1007/s11144-015-0892-6>  
IF: 1.265
2. **Fodor, T.**, Bányai, I., Bényei, A., Platas-Iglesias, C., Purgel, M., Horváth, G. L., Zékány, L., Tircsó, G., Tóth, I.: [TlIII(dota)]-: An Extraordinarily Robust Macrocyclic Complex. *Inorg. Chem.* **54** (11), 5426-5437, 2015. ISSN: 0020-1669.  
DOI: <http://dx.doi.org/10.1021/acs.inorgchem.5b00458>  
IF: 4.82





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**List of other publications**

Foreign language scientific articles in international journals (1)

3. Molnár, E., Camus, N., Patinec, V., Rolla, G. A., Botta, M., Tircsó, G., Kálmán, F. K., **Fodor, T.**,  
Tripier, R., Platas-Iglesias, C.: Picolinate-Containing Macrocyclic Mn(II) Complexes as  
Potential MRI Contrast Agents.  
*Inorg. Chem.* 53 (10), 5136-5149, 2014. ISSN: 0020-1669.  
DOI: <http://dx.doi.org/10.1021/ic500231z>  
IF: 4.762

**Total IF of journals (all publications): 10,847**

**Total IF of journals (publications related to the dissertation): 6,085**

The Candidate's publication data submitted to the iDEa Tudóstér have been validated by DEENK on the basis of Web of Science, Scopus and Journal Citation Report (Impact Factor) databases.

13 September, 2016



## V. List of publications

### V.1. Papers related to the thesis

4. Tamás **Fodor**, Zoltán Garda, Felicia Rozinka, Ferenc Krisztián Kálmán, Imre Tóth:

**Aminopolycarboxylate thallium(III) complexes as potential imaging radioisotope carriers**

(kézirat előkészítés alatt/manuscript to be written)

3. Wassim W. Ayass, Tamás **Fodor**, Zhengguo Lin, Rachele M. Smith, Linyuan Fan, Jie Cao, Imre Tóth, László Zékány, Magda Pascual-Borràs, Antonio Rodríguez-Forteza, Josep M. Poblet, and Ulrich Kortz:

**Introducing Thallium in Discrete Metal-Oxide Chemistry: The  $Tl^{3+}$ -Containing  $[Tl_2\{B-\beta-SiW_8O_{30}(OH)\}_2]^{12-}$ ,**

*Inorganic Chemistry* (beküldve/submitted) IF: 4.820 (2015)

2. Tamás **Fodor**, István Bányai, Attila Bényei, Carlos Platas-Iglesias, Mihály Purgel, Gábor Horváth, László Zékány, Gyula Tircsó and Imre Tóth:

**$[Tl(dota)]^-$ : An extraordinary robust macrocyclic complex**

*Inorg. Chem.*, **2015**, *54* (11), pp 5426–5437. IF: 4.762 (2014)

1. Edit Farkas, Tamás **Fodor**, Ferenc K. Kálmán\*, Gyula Tircsó and Imre Tóth:

**Equilibrium and Dissociation Kinetics of  $[Al(1,4,7\text{-triazacyclononane-1,4,7-triacetate})]$  ( $[Al(nota)]$ ) Complex,**

*Reaction Kinetics, Mechanisms and Catalysis*, **2015**, *116*(1), 19-33. IF: 0.983 (2013)

## V.2. Presentations related to the thesis

5. **Fodor** Tamás, Ayass W. W., Zékány László, Bodor Andrea, Kortz U., Tóth Imre: **Dimer vagy monomer?  $^{203/205}\text{Tl}$  NMR homo- és heteronukleáris spin-spin csatolások heteropolimetallátok oldataiban**

*50. Komplexkémiai Kollokvium*, Balatonvilágos, 2016. május 30-június 1,

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