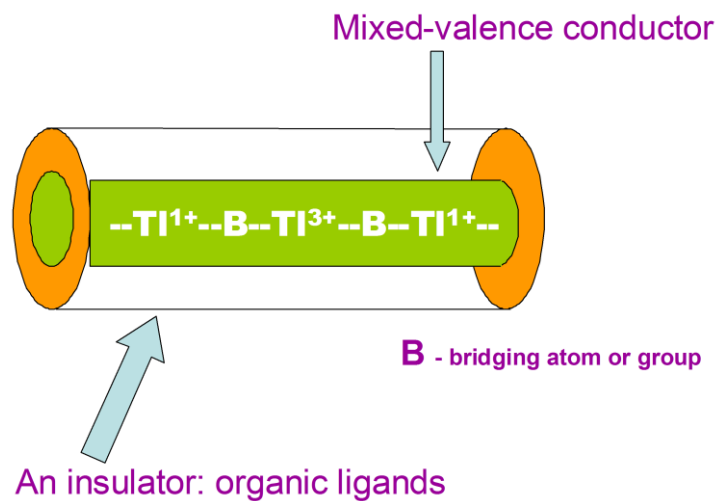




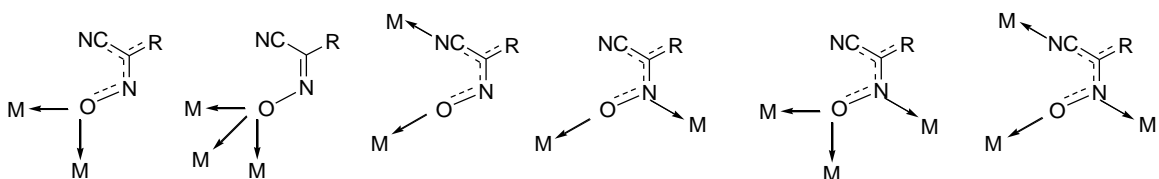
Daniel Robertson: MS 2006

Thesis "Thallium(I) Coordination Polymers Based on Monosubstituted Arylcyanoximes"

Daniel's research project was dedicated to the synthesis and characterization of a series of Tl(I) arylcyanoximates as suitable precursors for 1D mixed valence coordination polymers that may conduct electricity as shown below:



Daniel obtained and thoroughly characterized 9 monosubstituted arylcyanoximes that are shown in Figure 1. In these ligands by design we excluded the ability to form chelate complexes, but rather provided possibility for the formation of coordination polymers utilizing established very rich variety of bridging binding modes of the cyanoximes:



Presence of aromatic rings allowed for possible π - π stacking interactions that might stabilize lattice architecture, while presence of halogens on the ring would increase possibility for the extra-coordination by the halophylic monovalent thallium atoms.

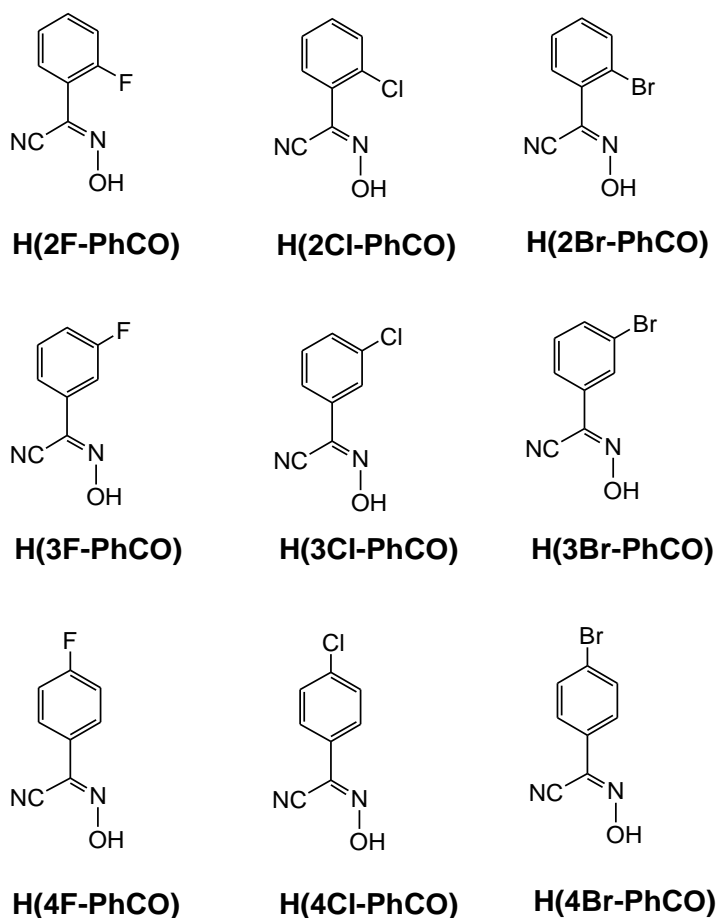


Figure 1. The list of cyanoxime ligands that were synthesized and studied by Daniel Robertson during his research in the group.

Design of new types of metal-organic networks and search for unusual crystal architecture represents an important task for modern inorganic and materials chemistry research. A group of new monosubstituted phenylcyanoximes, containing F, Cl and Br atoms at 2-, 3- or 4- positions, were synthesized using the high yield nitrosation reaction with $\text{CH}_3\text{-ONO}$, spectroscopically (^1H , ^{13}C , UV-visible, IR, mass-spectrometry) and structurally characterized. Results of x-ray analysis revealed non-planar *trans-anti* geometry for 2-chlorophenyl(oximino)acetonitrile, **H(2Cl-PhCO)**, non-planar *anti*-configuration for 4-chlorophenyl(oximino)acetonitrile, **H(4Cl-PhCO)**, and planar *cis-syn* geometry for 3-fluorophenyl(oximino)acetonitrile, **H(3F-PhCO)**. All arylcyanoximes undergo deprotonation in solutions with the formation of colored anions exhibiting pronounced *negative* solvatochromism in a series of polar protic and aprotic solvents. Nine thallium(I) cyanoximates were obtained using the reaction between hot ($\sim 95^\circ\text{C}$) aqueous solutions of Tl_2CO_3 and solid powdery monohalogenated arylcyanoximes HL. Crystal structures of two Tl(I) cyanoximates (**Tl(2Cl-PhCO)** and **Tl(4Br-PhCO)**) contained centrosymmetric dimeric units $(\text{TlL})_2$ that are connected to one-dimensional coordination polymer by means of an oxygen atom of the oxime group of the neighboring molecule. Cyanoxime anions act as bridging ligands in both structures where the polymeric motif consists of double-stranded Tl-O chains interconnected with the formation of zigzagging Tl_2O_2 planar rhombes. Thallium atoms form infinite linear arrays with close intermetallic separations. The nearest Tl(I)---Tl(I) distances are 3.838 Å and 4.058 Å in the **Tl(2Cl-PhCO)** and **Tl(4Br-PhCO)** structures respectively, close to that in metallic thallium (3.456 Å). Monosubstituted phenyl groups are well aligned in π -stacking columns that are perpendicular to the array of Tl(I) atoms and stabilize formed structures. Coordination polyhedrons of thallium(I) in these complexes represent distorted trigonal pyramids with stereoactive lone pair.

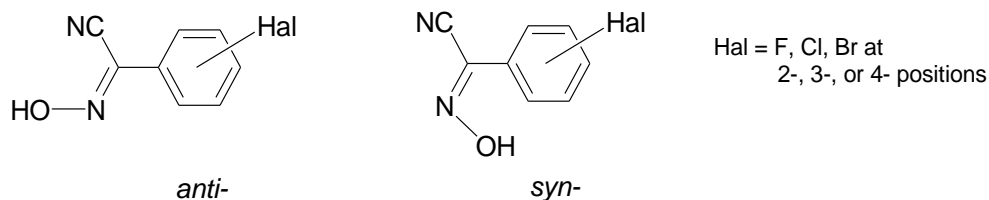


Figure 2. Most of the monosubstituted arylcyanoximes exist as a mixture of two geometrical isomers.

Contrary to 3 methods of synthesis of other cyanoximes developed in our research laboratory by Tiffany Maher (see her page in this section), only one method turned out to be feasible for the preparation of monosubstituted arylcyanoximes shown in Figure 1. That was the nitrosation reaction using either gaseous methylnitrite, $\text{CH}_3\text{-ONO}$, or freshly prepared in the lab alkylnitrites (not from ALDRICH!). Thus, our developed route is shown in Figure 3 below, while syntheses of Ti(I) salts are seen in Figure 4 below.

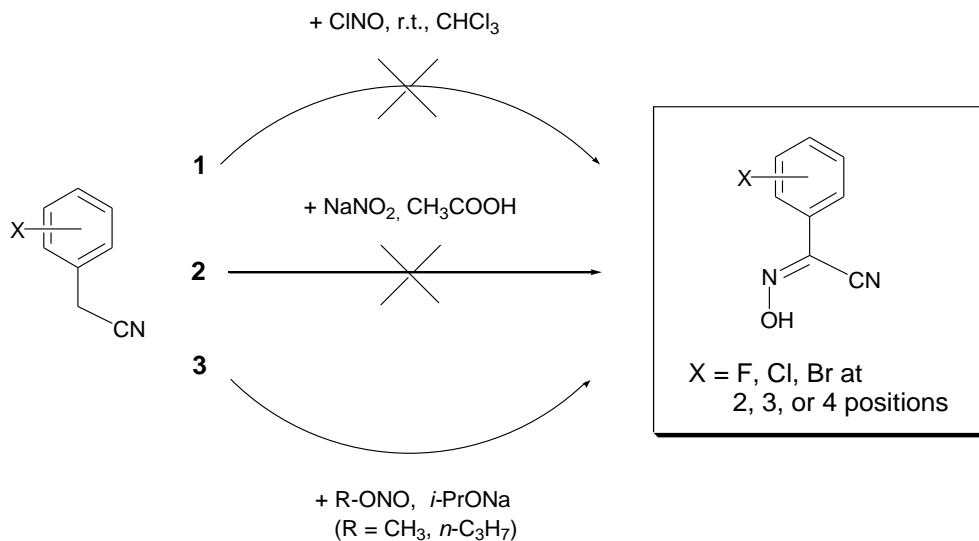


Figure 3. Method of high-yield preparation of the arylcyanoximes.

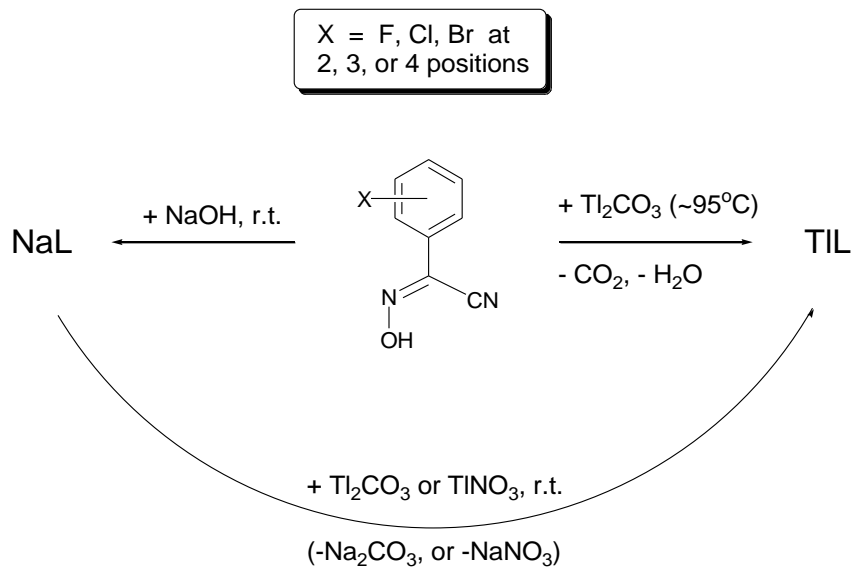


Figure 4. Route to Ti(I) coordination polymers.

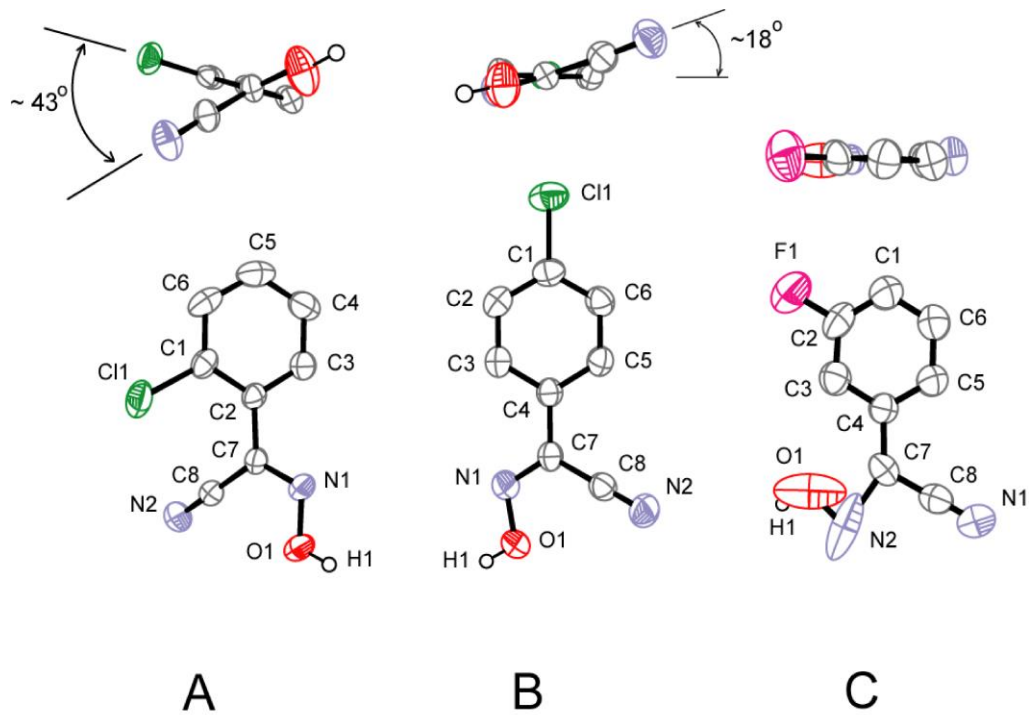


Figure 5. Molecular structures of several ligands used in his studies.

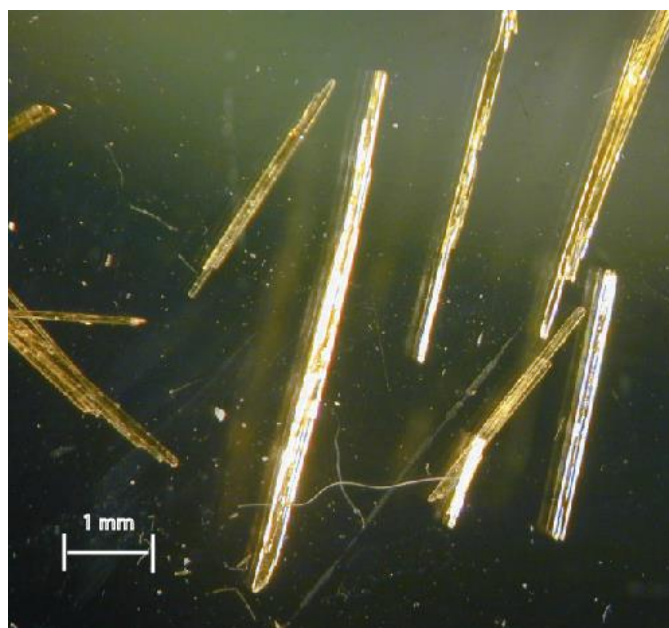


Figure 6. Actual photographs of long needles of $Ti(2Cl-PhCO)$ at x 40 magnification.

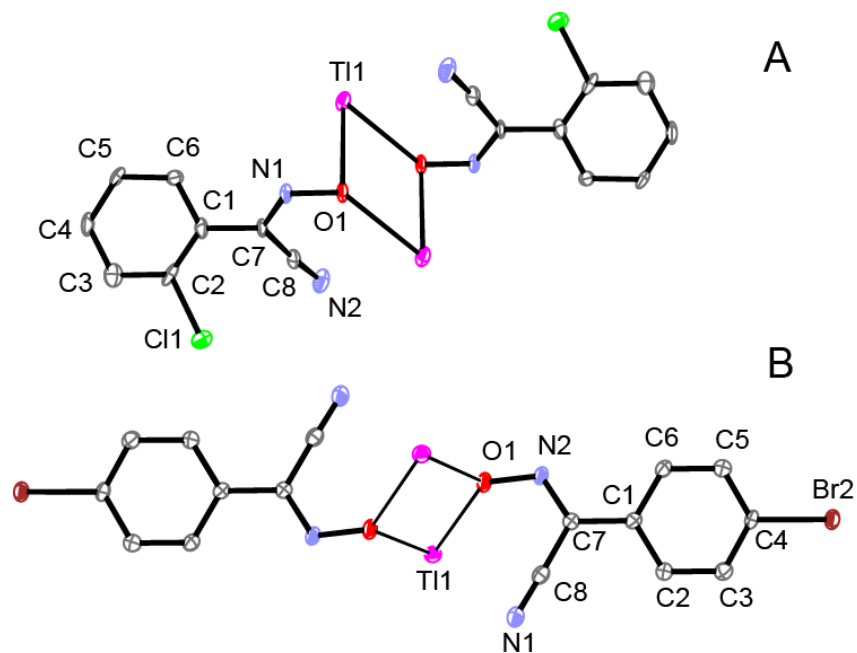


Figure 7. Molecular structures of centrosymmetric dimers of TI(2Cl-PhCO) (A) and TI(4Br-PhCO) (B).

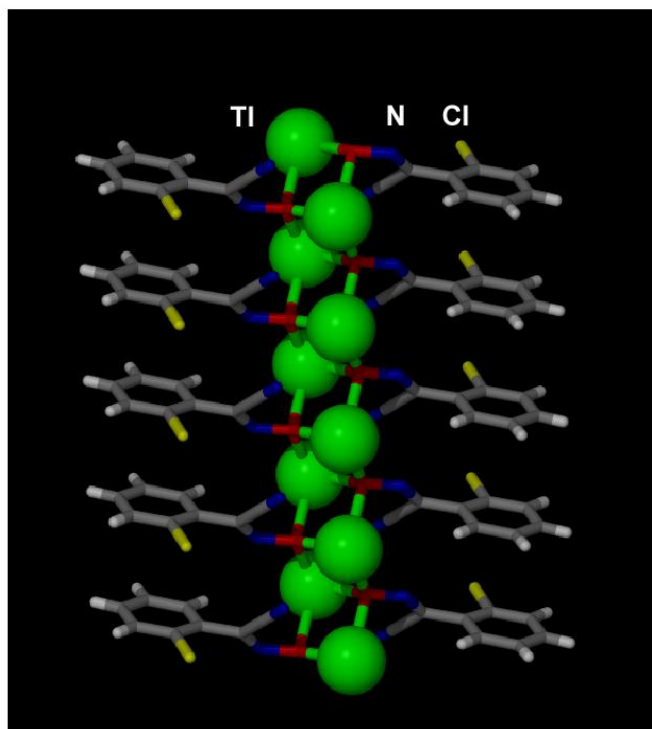


Figure 8. Capped-sticks view of structure of TI(2Cl-PhCO) showing π - π stacking stabilization of the lattice by 2-chloroaryl groups and close spatial location of metal ions (shown as wan-der-Waals spheres; green).

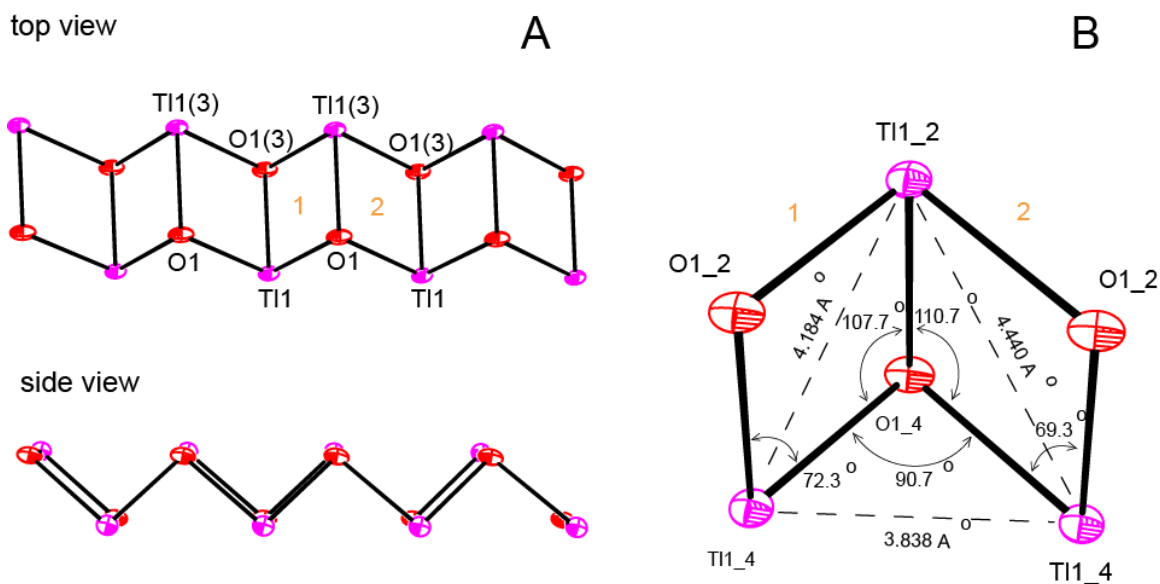


Figure 9. Structure of coordination polymer in $\text{Ti}(\text{2Cl-PhCO})$. A – double ladder that consists of two slightly different Ti_2O_2 rhombs; B – details of rhombs geometry.

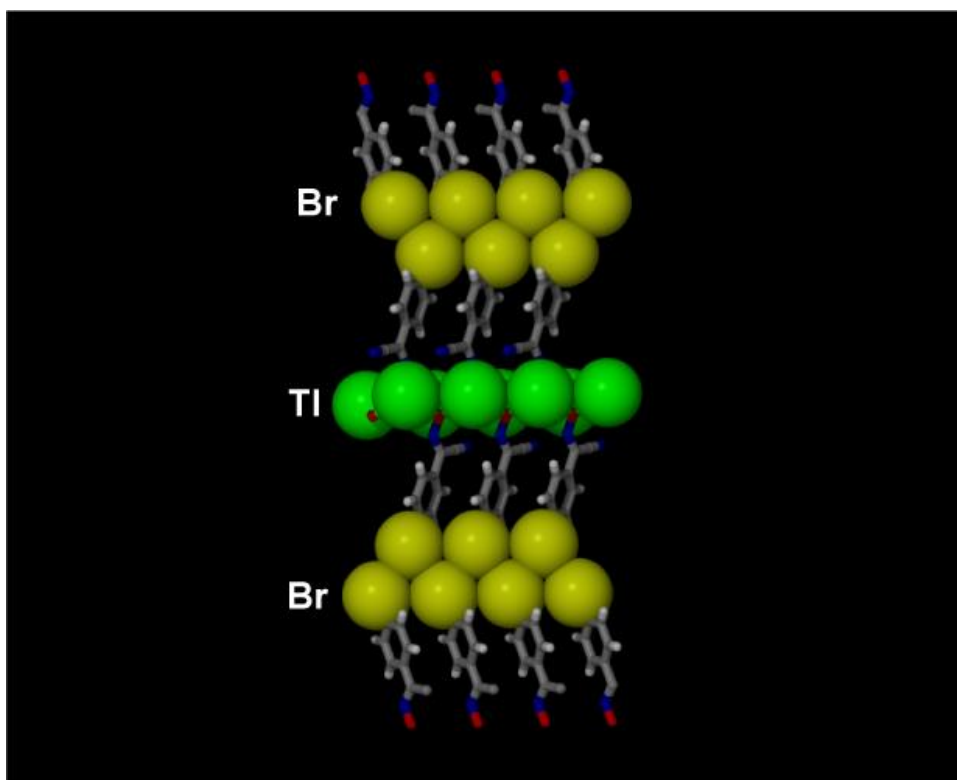


Figure 10. Capped-sticks view of structure of $\text{Ti}(\text{4Br-PhCO})$ showing π - π stacking stabilization of the lattice by 4-bromoaryl groups and close spatial location of metal ions (shown as wan-der-Waals spheres; green) and non-covalent $\text{Br}\cdots\text{Br}$ interactions (olive color).

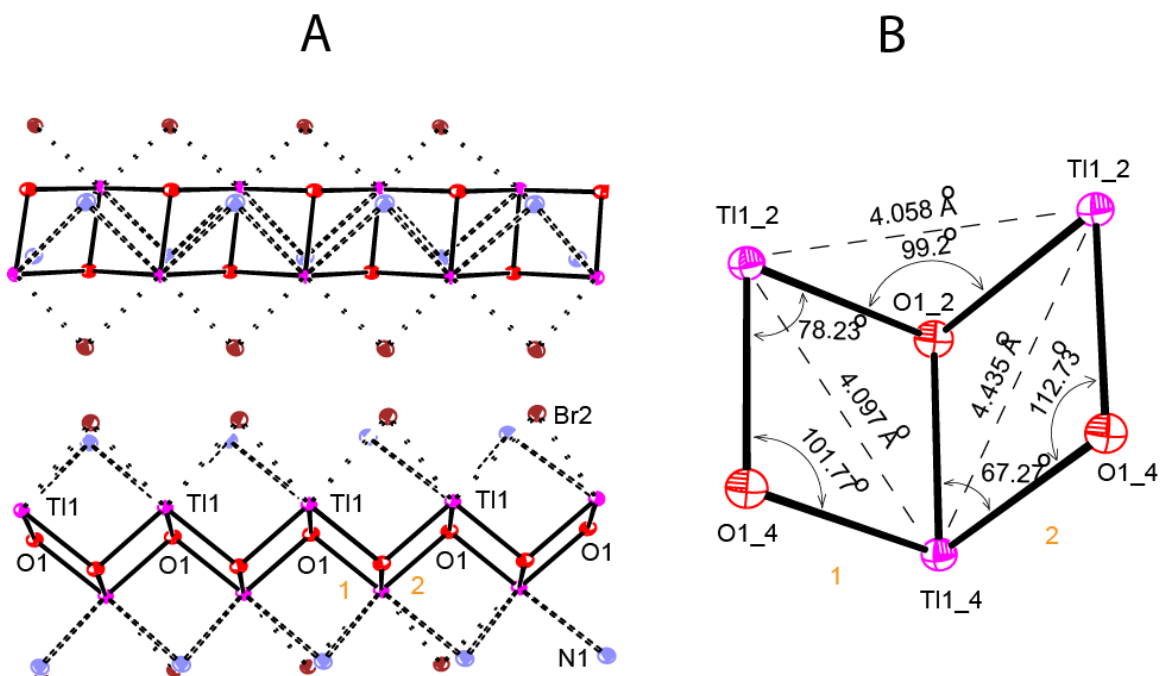


Figure 11. Structure of coordination polymer in $Ti(4Br-PhCO)$. A – double ladder motif that consists of two slightly different Ti_2O_2 rhombs; B – details of rhombs geometry.

Work of Daniel Robertson in my research group has resulted in two major peer-reviewed publications:

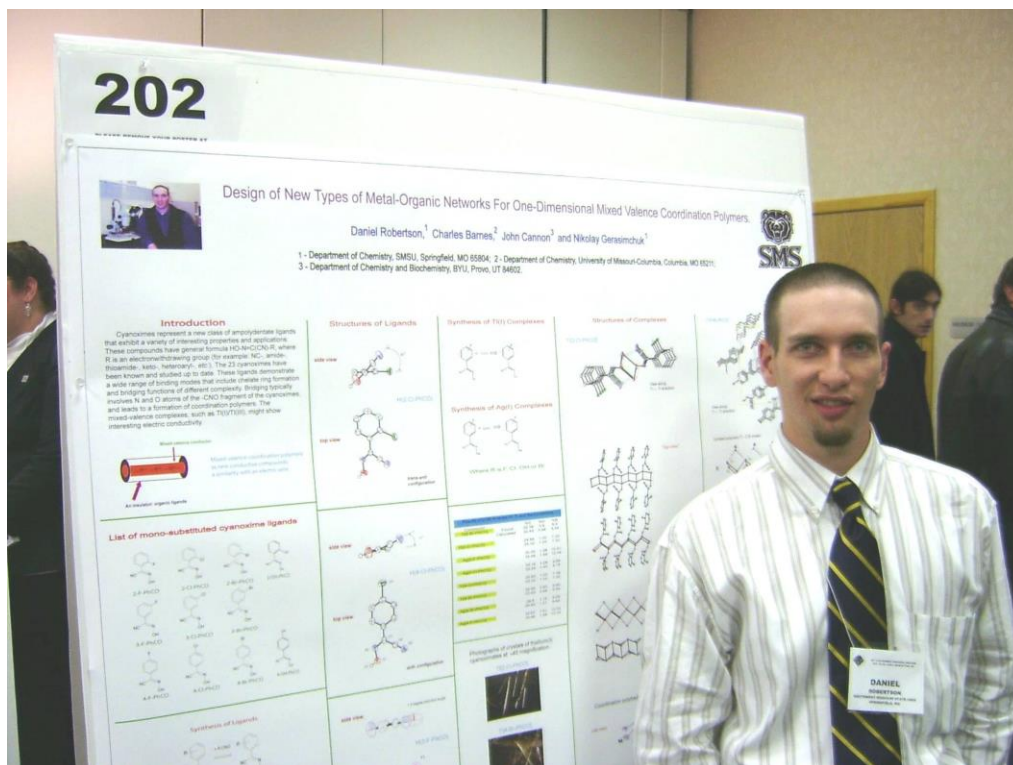
- 1) Robertson, D., Barnes, C., Gerasimchuk, N.N. "Synthesis of the monosubstituted arylcyanoxime and its Na, Ti(I) and Ag(I) compounds." *Journal of Coordination Chemistry* **2004**, 57, N°14, pp.1205-1216.
- 2) Robertson, D.; Cannon, J.F.; Gerasimchuk, N. "Double-Stranded Metal-Organic Networks for One-Dimensional Mixed Valence Coordination Polymers". *Inorganic Chemistry*. **2005**, 44, N°23, p.8326-8342.

and in 4 presentations at the regional and national meetings of the American Chemical Society:

1. Robertson, D., Barnes, C., Cannon, J., Gerasimchuk, N.N. "Synthesis and investigation of the first mono-substituted arylcyanoximes and their monovalent metal complexes." Proceedings of 38th Midwest Regional Meeting of the ACS; p. 187. Columbia, MO, 2003.
2. Robertson, D., Gerasimchuk, N., Cannon, J.F., Barnes, C. "Design of new types of metal-organic networks for one-dimensional mixed-valence coordination polymers." Proceedings of 39th Midwest Regional Meeting of the ACS; p. 213. Manhattan, KS, 2004.
3. Robertson, D., Cannon, J., Gerasimchuk, N. "First monosubstituted arylcyanoximes and their Tl(I) and Ag(I) complexes." Inorganic chemistry section, poster presentation. Fall 228 ACS Meeting, August, 22-26th; 2004, Philadelphia, PA.
4. Robertson, D., Cannon, J., Barnes, C., Gerasimchuk, N.N. "One-dimensional coordination polymers for molecular electronics." Inorganic chemistry section, poster presentation (721). Spring 229 ACS Meeting, March 13-17th, 2005, San Diego, CA.

Graduation DAY!





Presentation at the Regional Midwest ACS Meeting in Manhattan, KS (2004)



Presentation at the National ACS Meeting in Philadelphia, PA (2004)



A photo with Tiffany: survivors of the accident in the laboratory.



Presentation at the National ACS Meeting in San Diego, CA (2005)