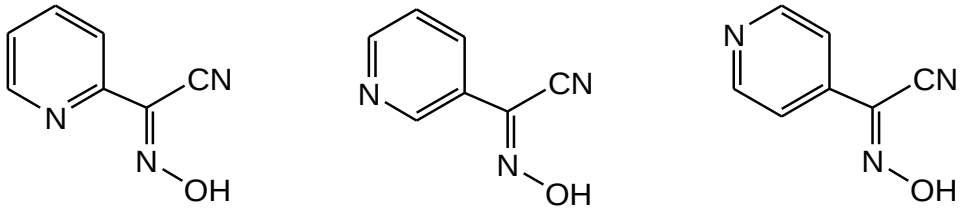
Daniela Marcano: MS 2007

Thesis “Pyridylcyanoximes and Their Metal Complexes”

Isomeric 2-, 3-, and 4-Pyridylcyanoximes, H(2PCO), H(3PCO), and H(4PCO), were synthesized via Meyer reaction from respective substituted pyridine-acetonitriles. Compounds were characterized by a variety of spectroscopic techniques such as ^{1}H, ^{13}C NMR, IR (including ^{15}N-labeling of the oximes and respective metal complexes) and UV-visible spectroscopy. In addition, crystal structures of H(3PCO) and H(4PCO) were determined and showed that both compounds exist as trans-*anti* isomers in solid state. A

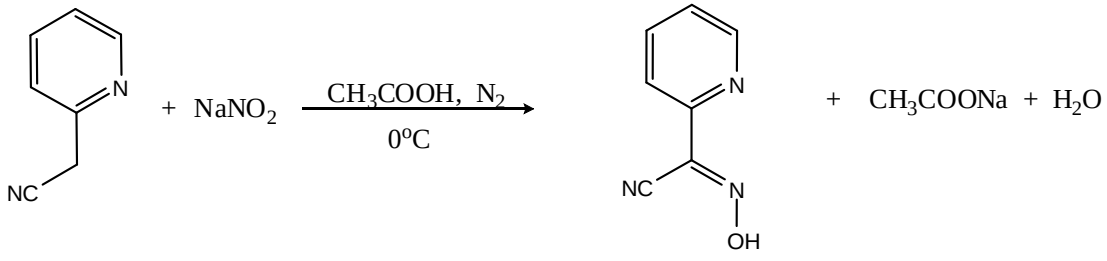
large group of coordination compounds of monovalent Na, Ag, Tl and bivalent Fe, Ni, Cu and Co was synthesized using deprotonated $[2PCO]^-$, $[3PCO]^-$, and $[4PCO]^-$ cyanoxe anions. The obtained complexes were characterized by IR, UV-visible spectroscopy. Crystal structures of the *mer*-isomer of $PPh_4[Ni(2PCO)_3]x2H_2O$, Tl(3PCO) and Tl(4PCO) were determined using X-ray analysis. Thus, results indicated that $[2PCO]^-$ behaves as chelating ligand in transition metals complexes where five-membered metallocycles are formed. Isomeric $[3PCO]^-$ and $[4PCO]^-$ anions act as bridging ligands using nitrogen atoms of the nitroso-, cyano-groups and heterocycle.

A series of Figures below provides illustration of key points of Daniela's research.



H(2PCO) **H(3PCO)** **H(4PCO)**

Figure 1. **Isomeric pyridylcyanoximes used in Daniela's research.**



H(2PCO)

Figure 2. **Synthesis of H(2PCO): conventional nitrosation at acidic conditions.**

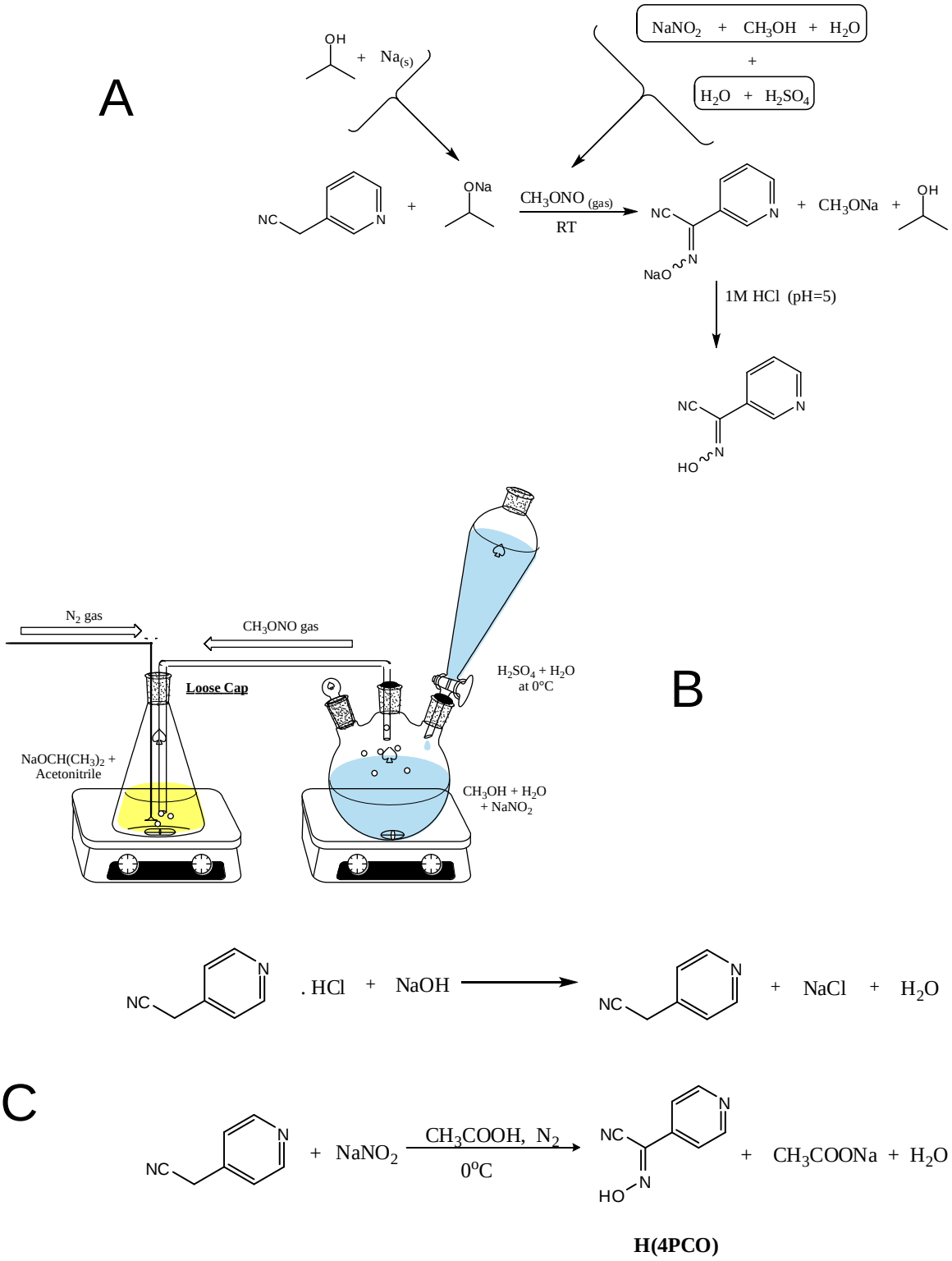


Figure 3. **Preparation of H(3PCO) – A, and B - showing experimental setup for generation of gaseous CH_3-ONO; two step reaction in synthesis of H(4PCO) - C.**

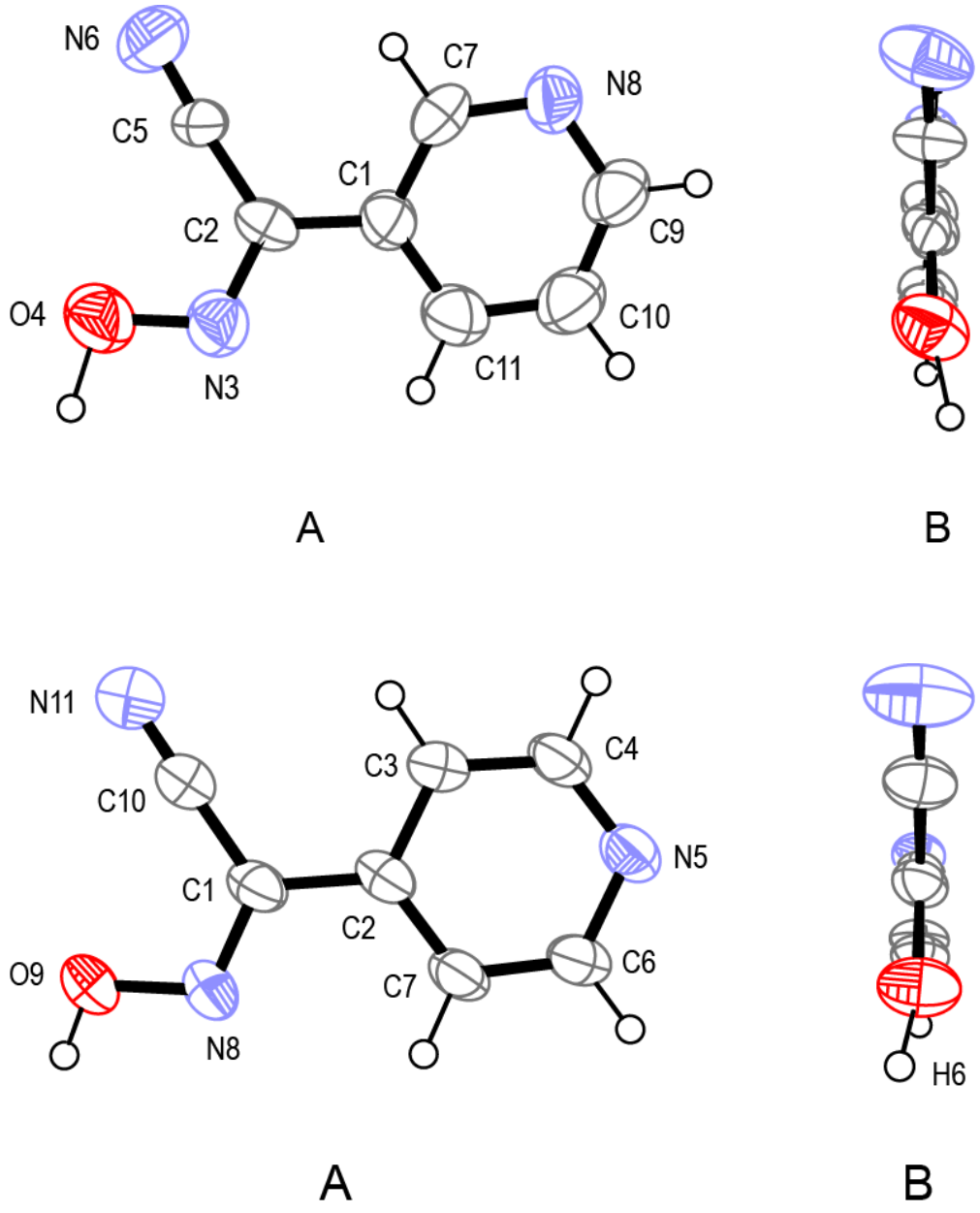


Figure 4. Molecular structures of H(3PCO) and H(4PCO): A – top views, B – side views showing ligand's planarity.

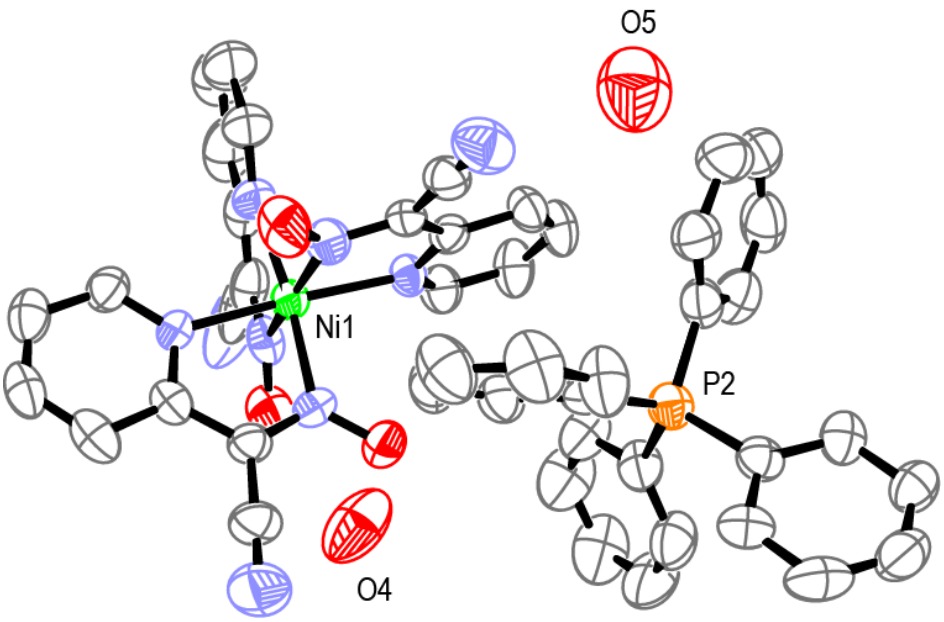


Figure 5. Molecular structure of *mer*-$PPh_4[Ni(2PCO)_3]\cdot 2H_2O$: an ORTEP representation at 50% thermal ellipsoids probability. H-atoms are omitted for clarity.

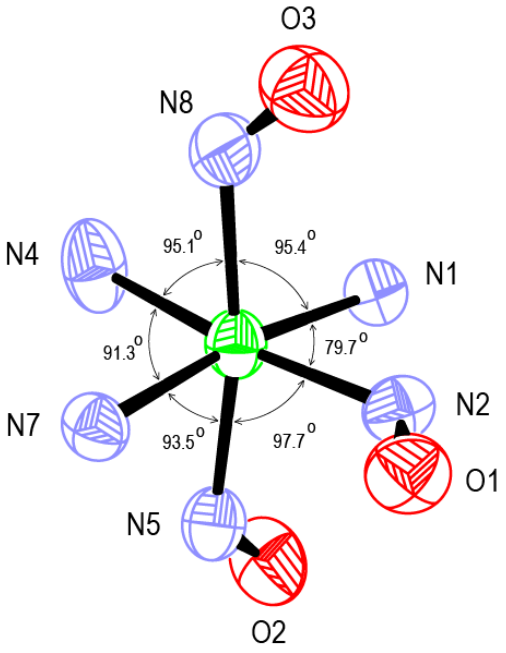


Figure 6. Geometry of coordination polyhedron in the structure of *mer*-$PPh_4[Ni(2PCO)_3]$. Other important parameters: <N4-Ni-N5 = 78.8°; <N8-Ni-N7 = 79.0°; <N1-Ni-N4 = 94.9°; Ni-N1 = 2.079Å; Ni-N2 = 2.016Å; Ni-N4 = 2.058Å; Ni-N5 = 2.088Å; Ni-N7 = 2.092Å; Ni-N8 = 2.076Å.

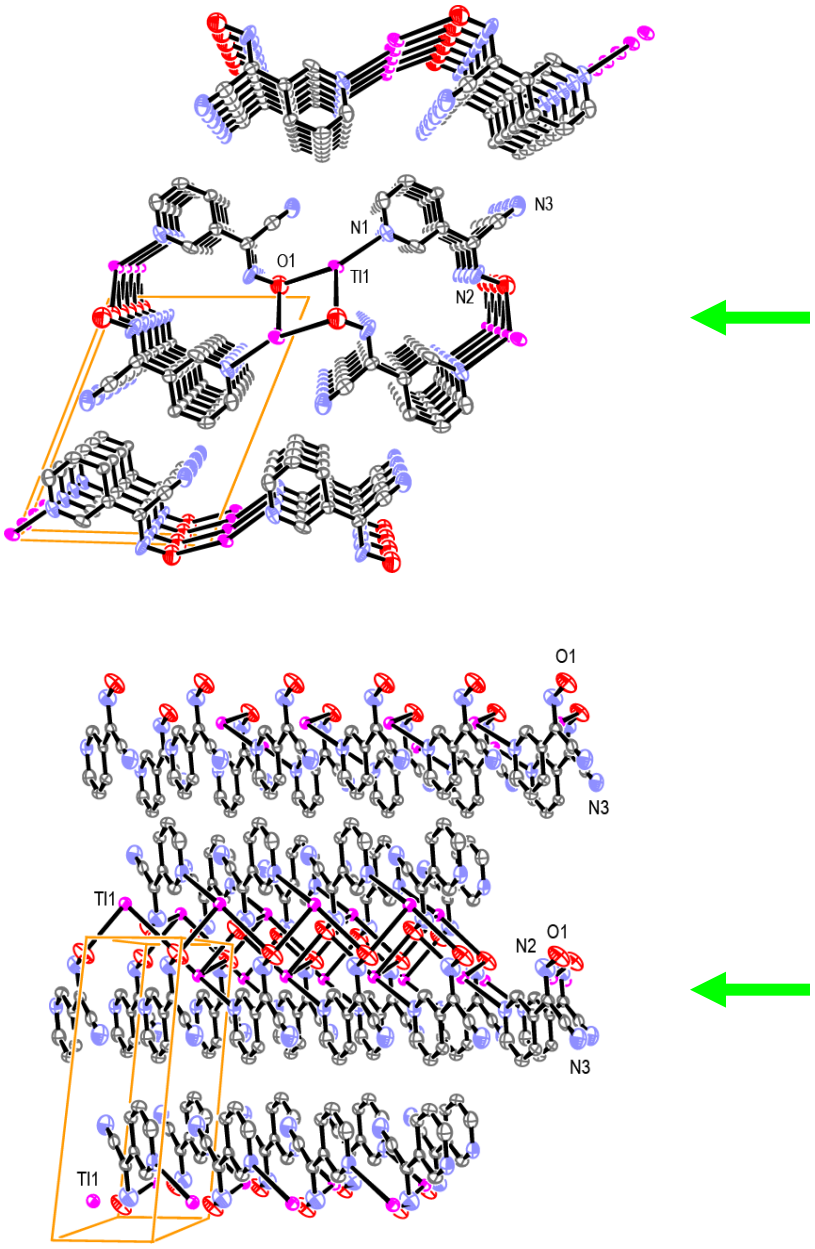


Figure 7. Organization of crystal structure of Tl(3PCO): two orthogonal projections. Shown formation of columns (green arrow) connected with each other by means of Wan-der-Waals forces.

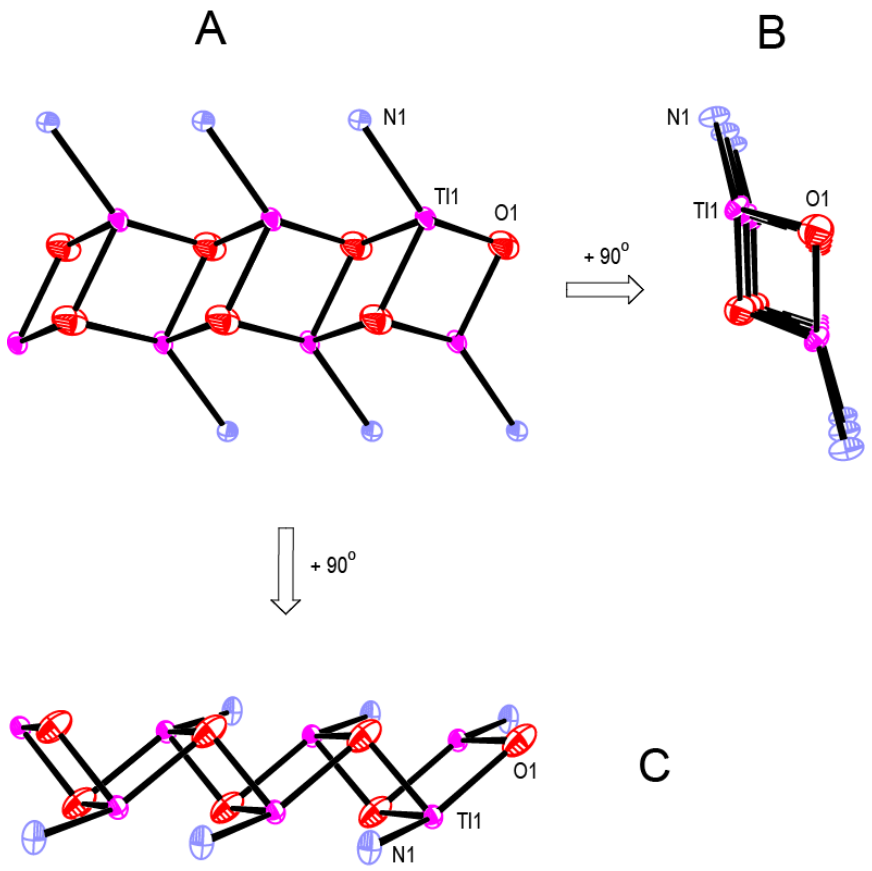


Figure 8. Three orthogonal projections of the double stranded (ladder) polymeric motif in 1D columns of Tl(3PCO). Shown numbering scheme helps to see 90° transformation. Coloring scheme: Tl – magenta; N – blue; O – red.

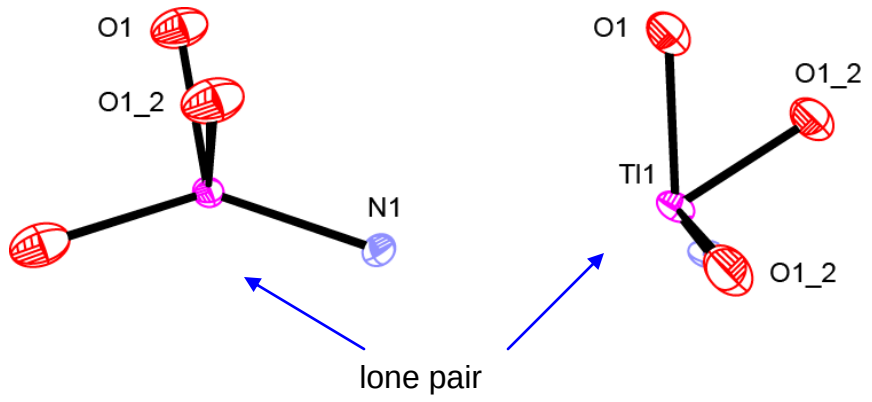


Figure 9. Coordination polyhedron in the structure of Tl(3PCO): distorted trigonal bipyramid (seesaw). Place for stereoactive $6s^2$ lone pair in an open cleft is indicated by arrows.

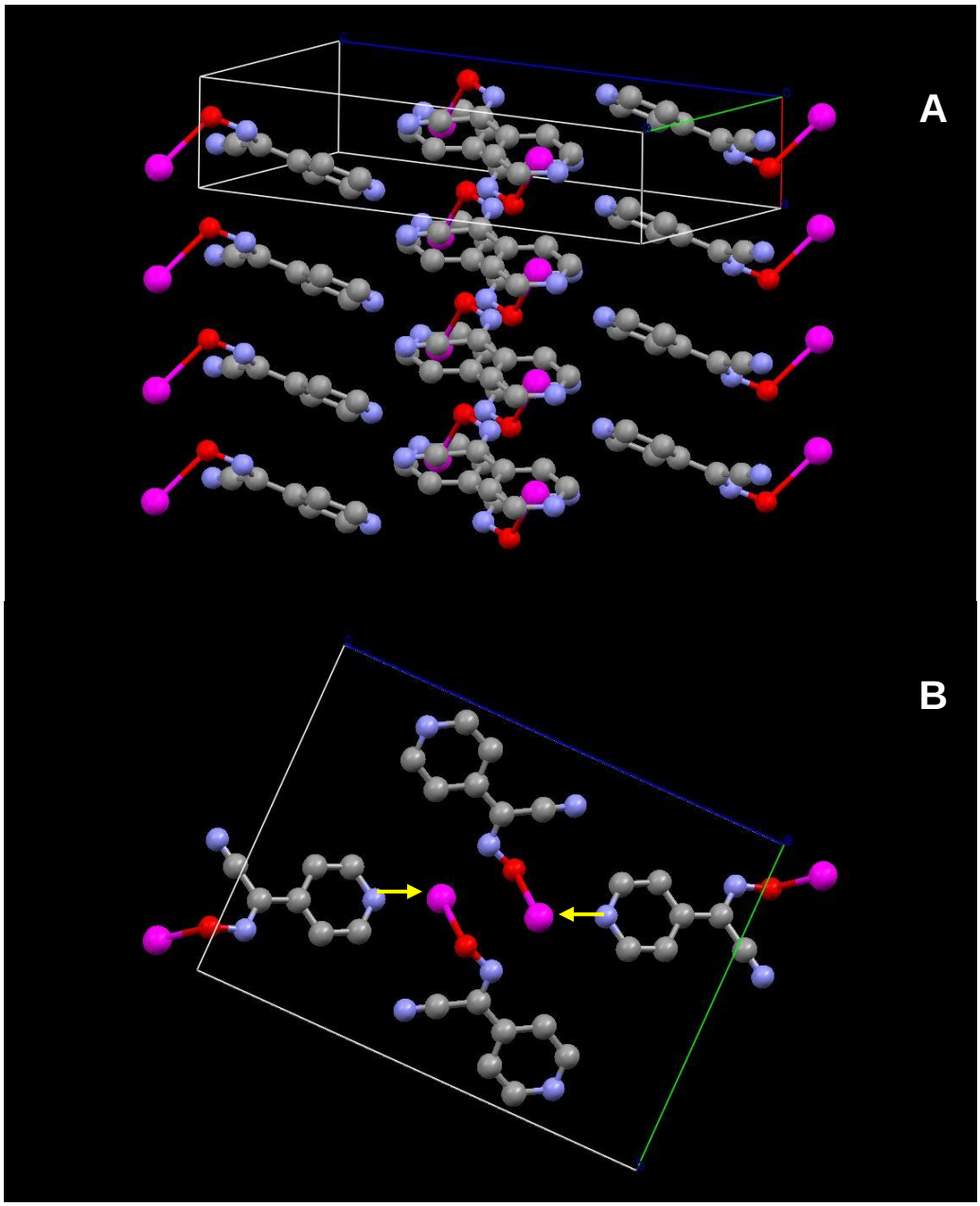


Figure 10. Organization of 3D polymeric structure of Tl(4PCO): two orthogonal views. 1D columns of complex (A) are connected into pleaded sheets by coordination of nitrogen atom of heterocycle to Tl(I) centers in the column (B) (shown as yellow arrows).
Coloring scheme: Tl- magenta; N – blue; O – red; C – grey.

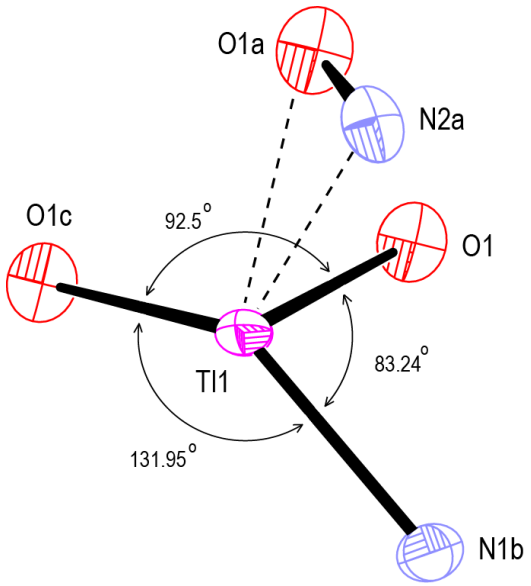


Figure 11. Structure of coordination polyhedron in Tl(4PCO): distorted trigonal pyramid capped with "side-on" coordinated oxime group from neighboring molecule. Lone pair occupies space between O1c and N1b atoms in an open cleft below Tl1. Coloring scheme: Tl – magenta; N – blue; O – red.

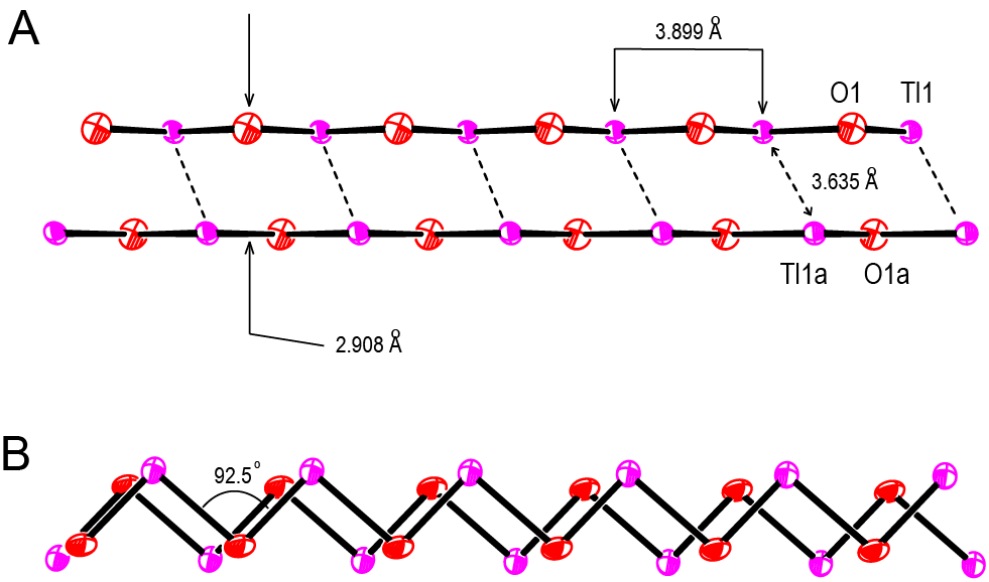


Figure 12. Two orthogonal views of zigzag Tl-O-Tl-O chains in 1D column of Tl(4PCO). Shown two short Tl---Tl distances in the structure, and separation of chains (2.908 Å) running is opposite directions.

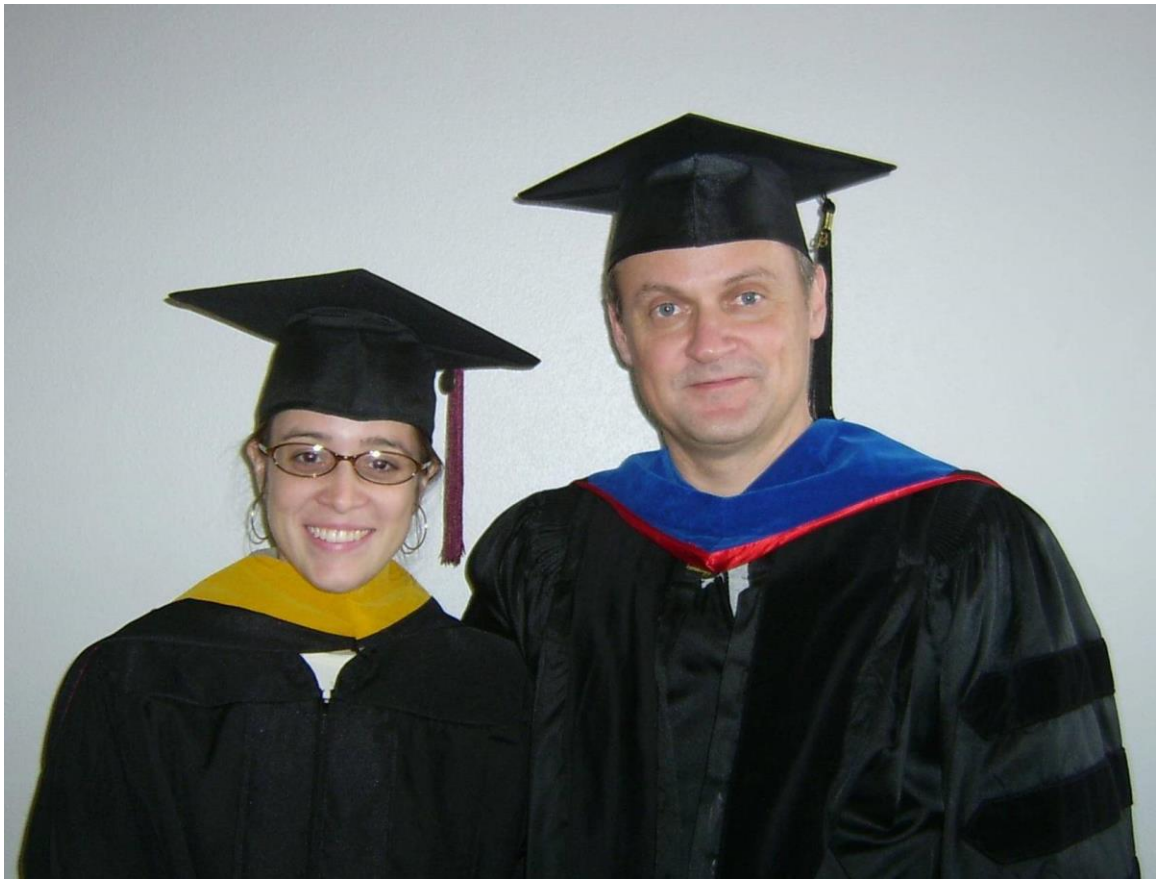
Work of Daniela Marcano in my research group has resulted in 2 presentations at the regional meeting of the American Chemical Society and Midwest Inorganic Chemists Association (MICA):

1. Marcano, D.; Nemykin, V.; Barnes, C.; Domasevitch, K.V.; Gerasimchuk, N. "Pyridylcyanoximes and their metal complexes". Proceedings of 42nd Midwest Regional Meeting of the ACS, p.139; November 7-10th, 2007; Kansas City, MO.

2. Marcano, D. "Pyridylcyanoximes and their 3d-metal derivatives"; Fall MICA Meeting, Harding University, Searcy, AR; October 7th, 2007.

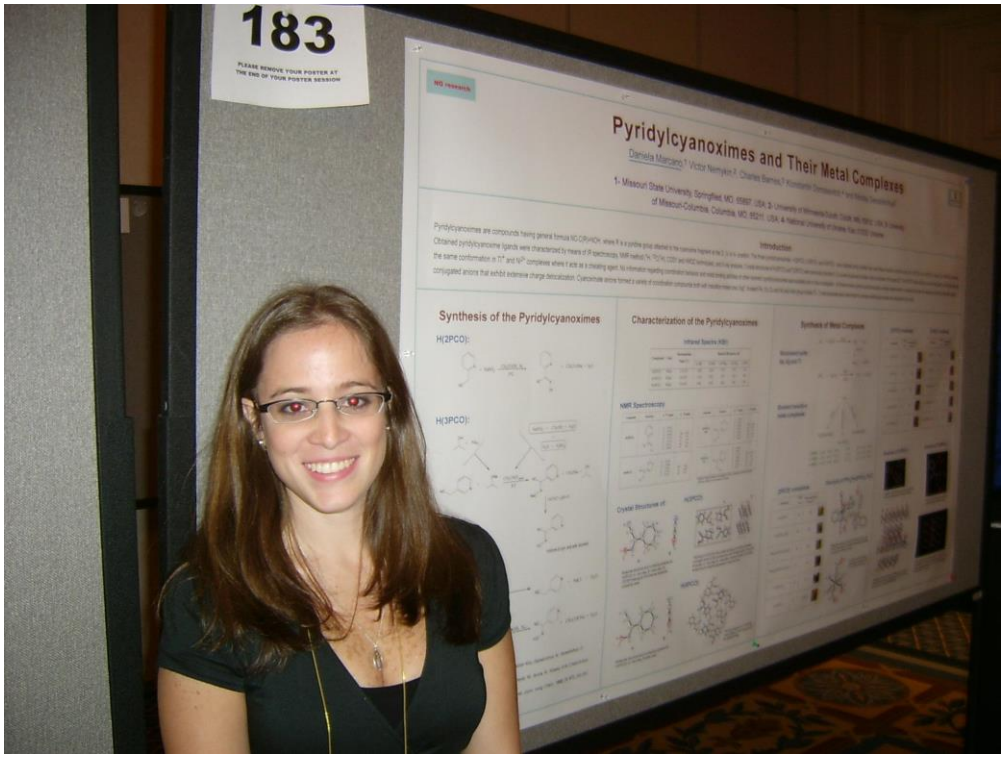
Two major peer-reviewed papers were also published:

1) **D. Marcano**, N. Gerasimchuk, V. Nemykin, and S. Silchenko. "Synthesis, Characterization and Studies of Coordination Polymers With Isomeric pyridylcyan-oximes: Route to Metal Ribbons With Very Short Tl---Tl separations." *Cryst. Growth & Des.*, **2012**, *12*, p.2877-2889.
2) **Marcano, D.C**.; Lindeman, S.V.; Pyrkosz-Bulska, M.; Gumienna-Kontecka, E.; Lengyel, A.; Kuzmann, E.; Röminger, F.; Gerasimchuk, N. "The 2-Pyridylcyanoxime and its Complexes." *Current Inorganic Chemistry*, **2015**, *5* (2), p.98-113.



Graduation!

In the lab where she spent 2 years…



At the poster on Regional ACS Meeting in Kansas City, 2007

Blowing glass in CHM 597 Summer Intersession class.

Spring 2007 Departmental Graduation Dinner where Daniela received an award.

After Fall 2007 MICA Meeting in Searcy, AR