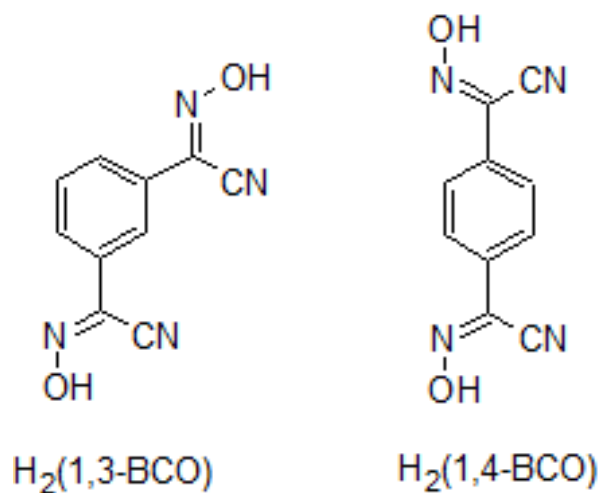


Scott Curtis: 2013

Thesis

“Synthesis and characterization of the first non-chelating bis-cyanoximes and their metal complexes.”

Research project of Scott Curtis was dedicated to the synthesis and characterization of two new non-chelating bis-cyanoximes (shown below) and their investigation as bridging dianionic ligands for coordination chemistry applications.

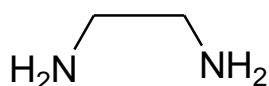


ABSTRACT

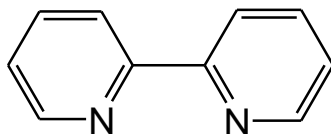
The first non-chelating phenyl bis-cyanoximes ($H_2(1,3\text{-BCO})$ and its isomer $H_2(1,4\text{-BCO})$) were synthesized and characterized by FT-IR spectroscopy, 1H , ^{13}C , 1H - 1H COSY NMR spectroscopy, UV-visible spectroscopy and X-ray analysis. $H_2(1,3\text{-BCO})$ adopts four primary configurations as was confirmed by NMR analysis. Both ligands undergo deprotonation and form planar anions which exhibit solvatochromism in a variety of protic and aprotic solvents. A variety of new complexes, a series of monovalent Ag, Tl, and bivalent Cu and Ni complexes was prepared and characterized. Tl(I) complexes display short Tl—Tl interatomic distances, one exhibits porous channels. Ag(I) complexes are highly light-sensitive. Attempts were made to synthesize metal complexes using metalloligands of the formula $[M(\text{Am})_n\text{X}_2]$ ($M = \text{Cu}, \text{Ni}$; $\text{Am} = 1,2$ -diaminomethane, 2,2'-dipyridyl and 1,10-phenanthroline; $n = 2,3$; $\text{X} = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-$) Three of four 3d-metal complexes were found to contain trapped solvent molecules in their crystal structures. One of the complexes synthesized, $[\text{Cu}(\text{En})_2(1,3\text{-BCO})]$, exhibited binding of the cyano group to the Cu atom and was found to possess open space in its crystal structure.

KEYWORDS: Bis-cyanoximes, supramolecular chemistry, coordination polymers, metal complexes, transition metals.

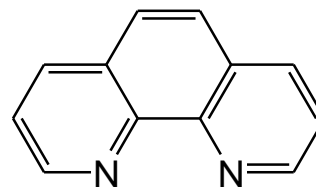
In order to achieve set in these study goals, it was necessary to obtain several metallo-ligands – complexes that contain transition metals of interest and have 4 out of 6 coordination sites blocked by “dummy” neutral ligands – and then react those with newly obtained bis-cyanoximes. The best choice for neutral strong metal binding ligands is using bidentate diamines such as 1,2-diaminoethane (**En**), as well as classic heterocyclic chelators **Dipy** and **Phen** displayed below.



En



2,2'-dipy (or Dipy)



1,10-phen (or Phen)

Two selected for this investigation deprotonated dianionic bis-cyanoximes itself allow adaptation of either 180° or 120° linkage between cationic species. However, being a part of the coordination compound with the above “dummy” ligands there are two distinct geometrical orientations in polymeric complexes formed. Thus, the first ligand **En** can form both cis- and trans complexes as shown in Figure 1 with 180° and 90° apart extension of the polymeric motif.

Cis- or Trans Motif

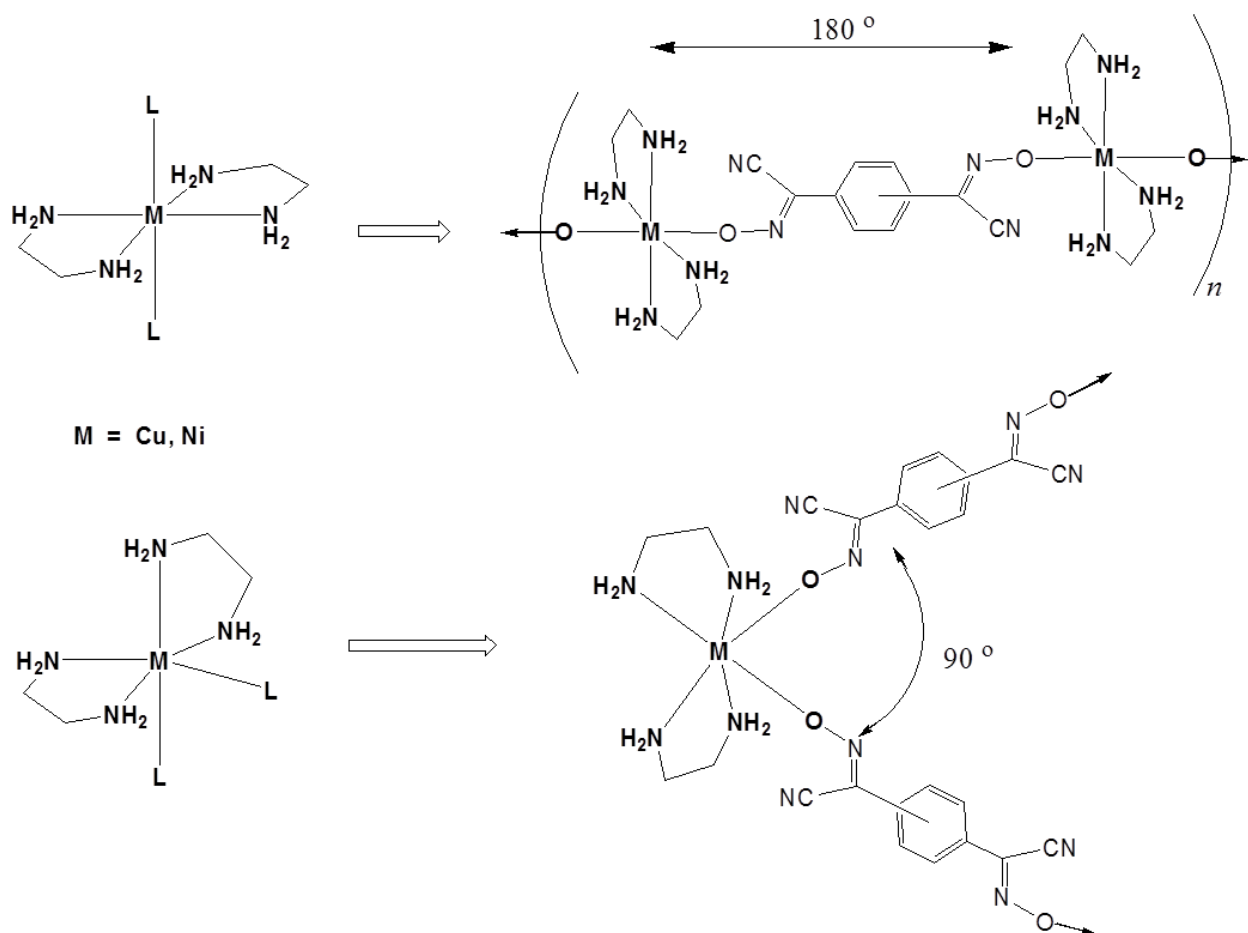


Figure 1.

At the same time with bulky heterocyclic diamines **Dipy** and **Phen** only cis-orientation is possible as explained in Figure 2.

The main advantage and beauty of such design is an introduction of dianionic bis-cyanoxime, which alleviates completely the necessity for the counter anions in classic coordination polymers formed by neutral chelating amino-ligands with transition metal cations.

Cis-Only Motif

M = Cu, Ni; dipy, phen complexes: *cis*- only!

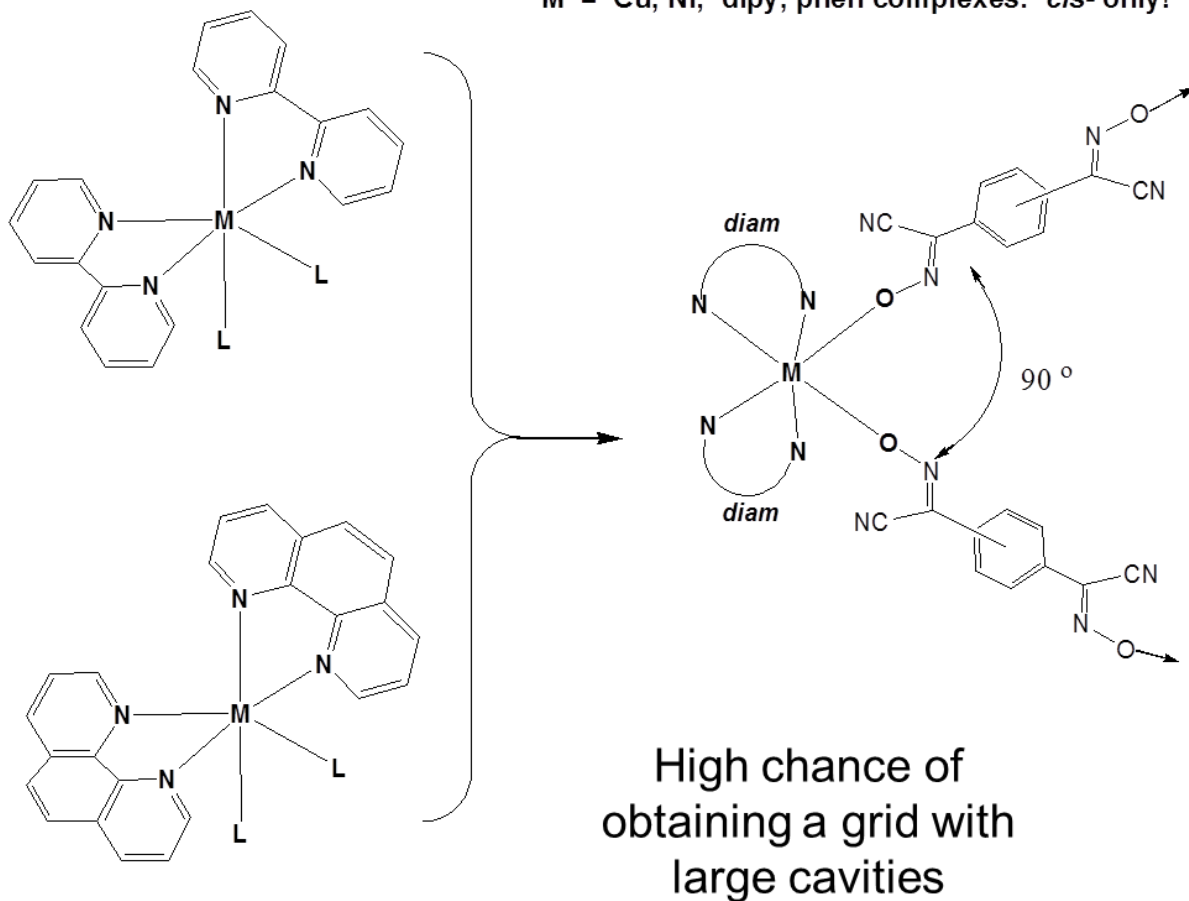


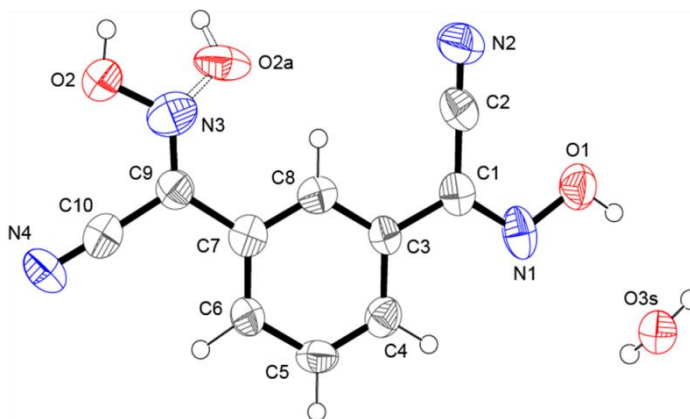
Figure 2.

Major accomplishments of Scott Curtis are presented below.

1. Two new phenyl bis-cyanoximes were successfully synthesized.
2. The new bis-cyanoximes were characterized by elemental analysis, IR spectroscopy, UV/Visible spectroscopy, NMR spectroscopy, and X-ray analysis. Structures are shown below in Figure 3.

F d d 2
R = 0.06
GOF = 1.037

85% *Syn* Isomer
15% *Anti* Isomer



P-1
R1 = 0.0270
GOF = 1.070

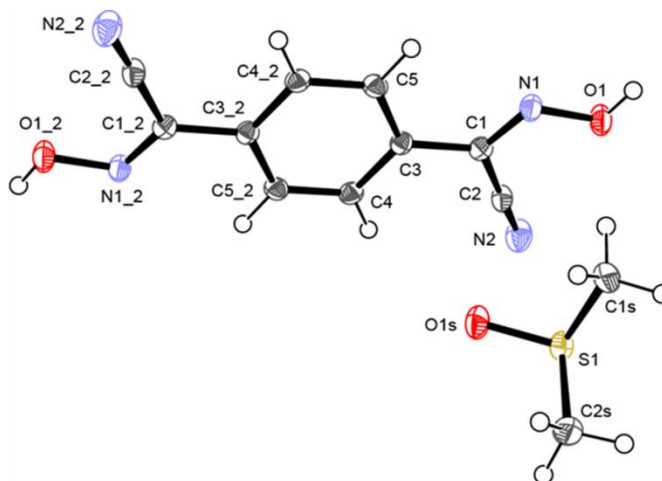


Figure 3.

3. The new bis-cyanoximes exhibit weak negative solvatochromism in solution.
4. Monovalent Ag(I) and Tl(I) complexes were synthesized. The structure of Tl₂(1,3-BCO) contains porous channels 6.55 Å across. This fact represents a first success in making a cyanoximate with porous channels (Figure 4).
5. The Ag(I) complexes of both cyanoximes are highly light-sensitive.
6. The Tl₂(1,4-BCO) crystallizes with a “zig-zag” pattern in also forms the Tl₂O₂ coordination polyhedron (Figure 5).

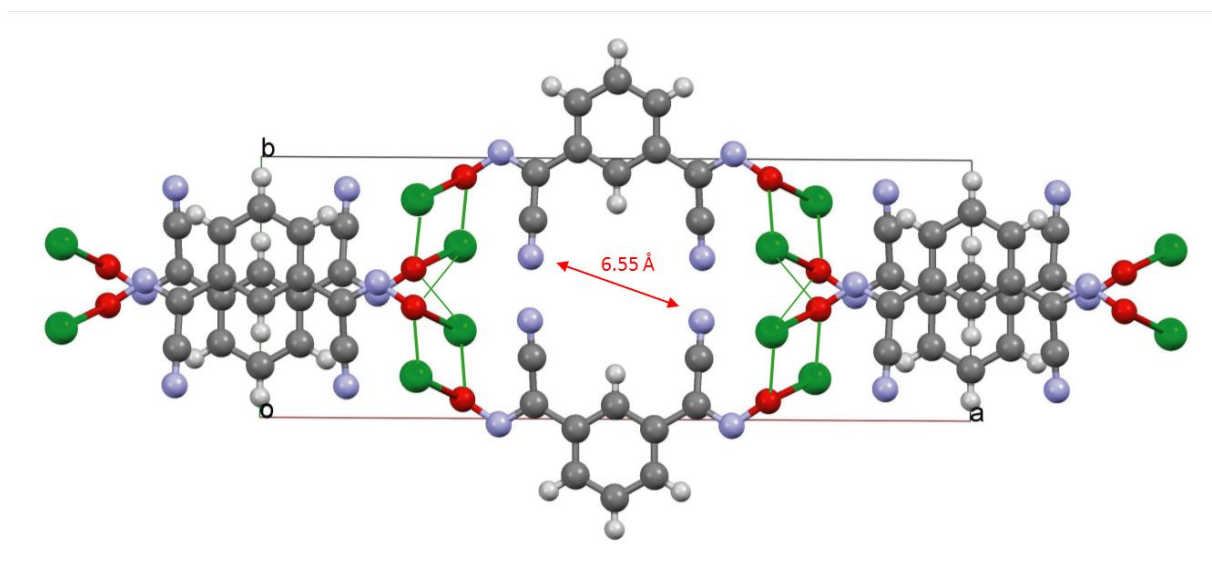
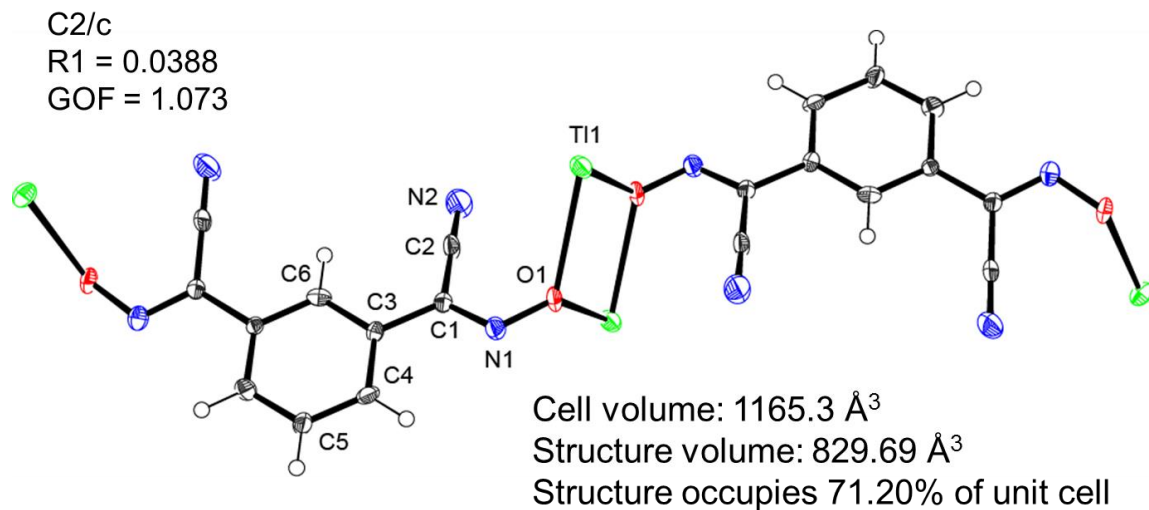
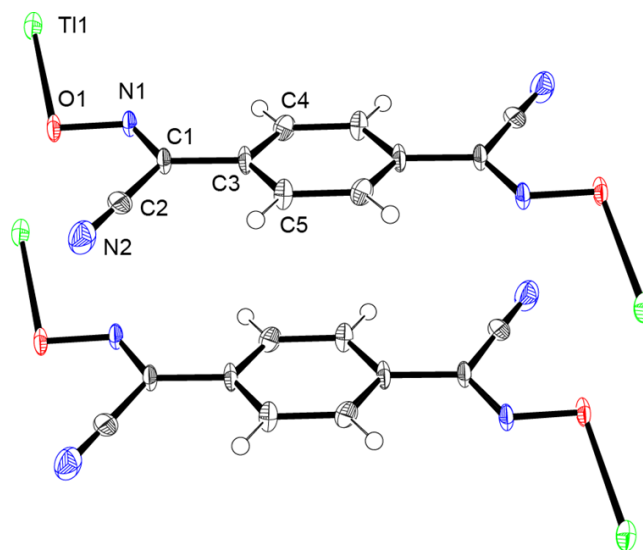


Figure 4.

7. Metalloligands of the general formula $M(\text{Am})_n\text{X}_2$ ($M = \text{Cu}^{2+}, \text{Ni}^{2+}$; $\text{Am} = \text{En}, \text{Dipy}, \text{Phen}$, $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$; $n = 2,3$) were synthesized and characterized by elemental analysis, IR spectroscopy, and X-ray analysis.
8. Attempts were made to synthesize extended lattice structures with our new cyanoximates and these metalloligands. This attempt was unsuccessful, however four complexes were successfully characterized, three of which contained $[\text{M}(\text{Am})_3]^{2+}$.

P-1
R1 = 0.0402
GOF = 1.035



Cell volume: 290.73 Å³
Structure volume: 205.8 Å³
Structure occupies 70.8% of unit cell

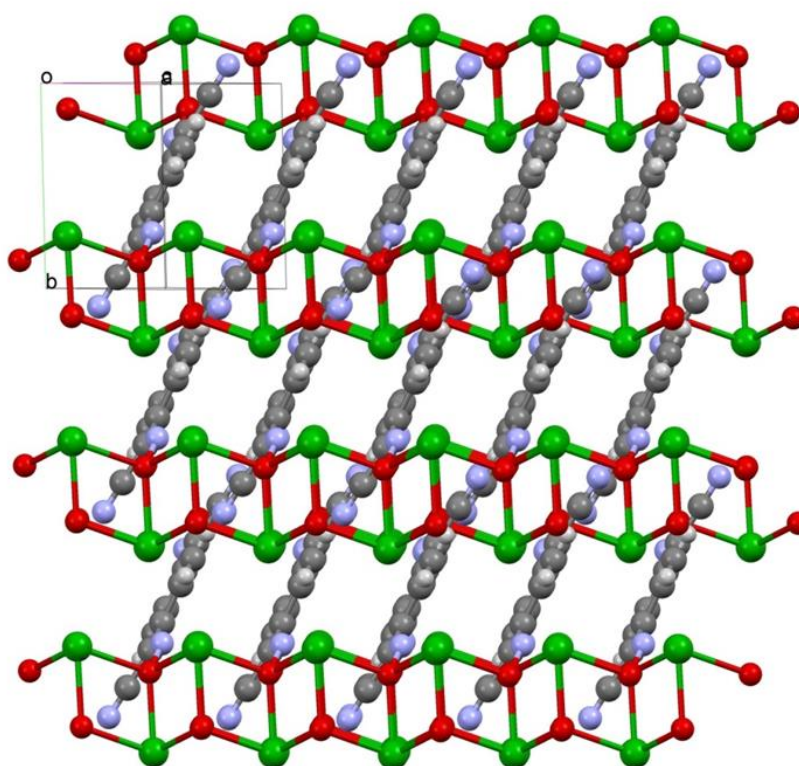


Figure 5.

One major peer-reviewed publication with Scott Curtis:

- 1). Curtis, S.; Ilkun, O.; Brown, A.; Silchenko, S.; Gerasimchuk, N. "Synthesis, spectroscopic and structural characterization of the first phenyl bis-cyanoximes: non-chelating extended ionisable building block ligands for new MOFs." *Cryst. Eng. Comm.* **2013**, *15*, p.152-159

Conference presentations with Scott Curtis:

47th Midwest Regional ACS Meeting (October 24-27, 2012; Omaha, NE)

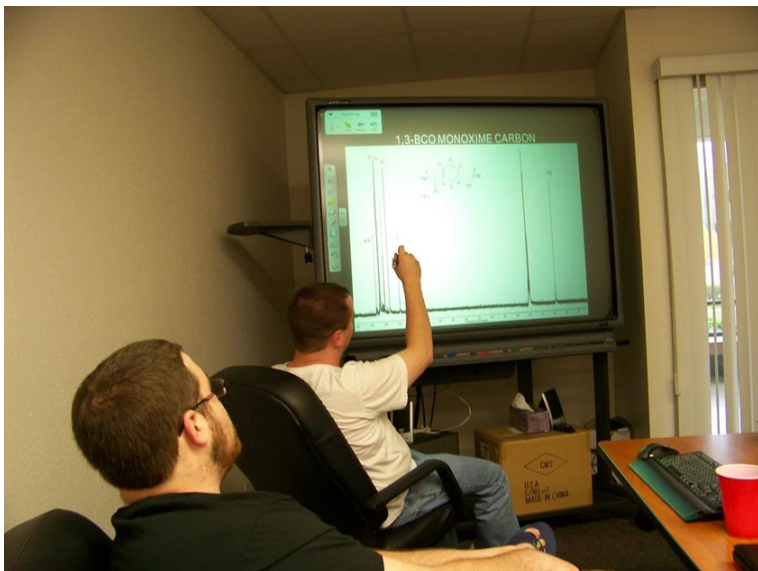
Curtis, S. M.*; Gerasimchuk, N.; Ilkun, O.; Brown, A. "First bis-cyanoximes: synthesis, spectroscopic studies, metal complexes, and coordination polymer studies." Abstracts, 47th Midwest Regional Meeting of the American Chemical Society, Omaha, NE, United States, October 24-27, MWRM-319.

Spring 2012 National Meeting of the ACS:

Curtis, S.*; Gerasimchuk, N.; Ilkun, O.; Brown, A. "First bis-cyanoximes: Synthesis, spectroscopic studies, crystal structures, and alkaline metals complexes" Abstracts of Papers, 243rd ACS National Meeting, San Diego, CA, USA, March 25-29, 2012, INOR-796.

40th International Conference on Coordination Chemistry (Valencia, Spain; September of 2012).

Curtis, S.*; Cheadle, C.*; Ilkun, O.; Gerasimchuk, N. "First Bis-Cyanoximes: New Versatile Multidentate Building Blocks for MOFs." Poster presentation at ICC-40, September 9th-13th, 2012.



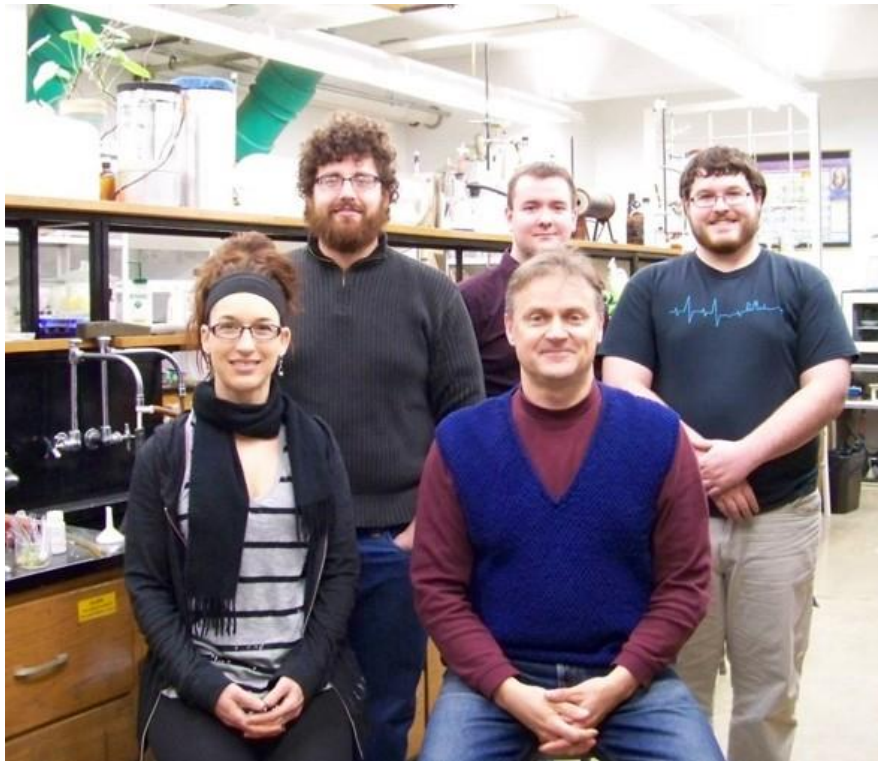
Scott presents at a group meeting.

During Scott Curtis stay in my research group we had some extensive travel together. Thus, we participated in several regional, national and even international conferences. Some photos from that time are presented below.

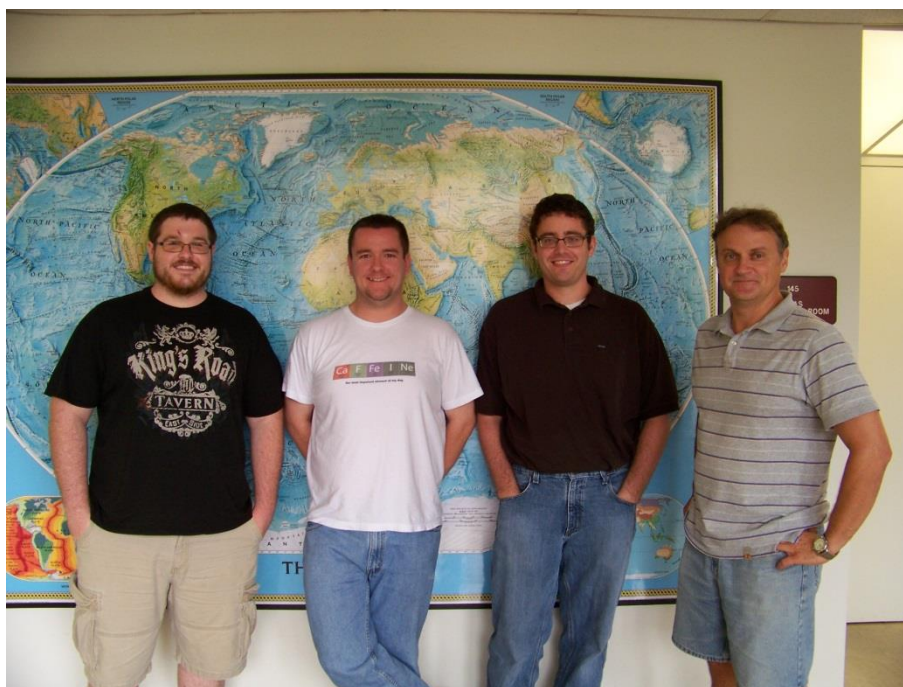
2011: travel to Bruker Users Meeting in Madison, Wisconsin.



2012: group picture in Temple 431 – research laboratory.



2012: research group picture in Temple Hall.



2012, March: research group travels for the National ACS meeting in San Diego (CA).



In Balboa Park



Walk on the Mission Beach



Visiting point Loma historical monument overlooking San Diego Bay, Coronado Island and Naval Base.



Graduation!