

Garrett Glover, 2006 - 2008

Garrett Glover worked in the research group for three years being enrolled in CHM 399 (2 hours) and CHM 499 (3 hours) research classes, and also as a research assistant for one of the grants. His research project was dedicated to synthesis, characterization and photophysical studies of a series of visible light insensitive Ag(I) complexes with cyanoximes shown in Figure 1 below. This is a remarkable property in context of well known application of Ag(I) salts in conventional photography.

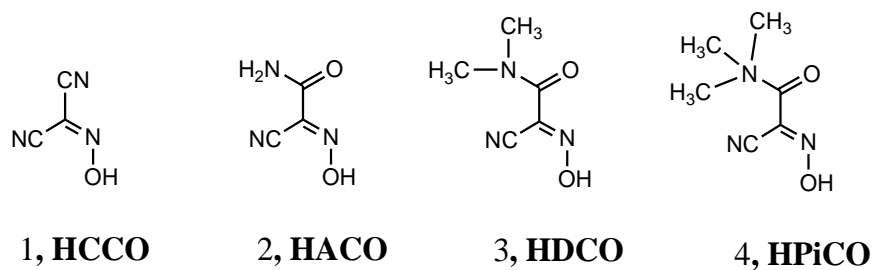


Figure 1. Cyanoxime ligands used in Garrett's research project.

Four K, Cs, Ag(I) and Tl(I) compounds with nitrosodicyanomethanide $\text{ONC}(\text{CN})_2^-$ anion (Figure 1: CCO^-) have been obtained (Figure 2) and characterized using IR spectroscopy (Figure 4), UV-visible spectroscopy (Figure 3), room temperature solid state photoluminescence and solutions electrical conductivity measurements. Cesium and thallium(I) complexes were obtained for the first time, and crystal structures were determined for $\text{Cs}\{\text{ONC}(\text{CN})_2\}$, $\text{Ag}\{\text{ONC}(\text{CN})_2\}$ and $\text{Tl}\{\text{ONC}(\text{CN})_2\}$. These structures indicate the formation of completely different 3D polymeric networks in which the anion acts as bridging ligand of different capacity. The cyanoxime ligand in all complexes studied is in *nitroso* form and adopts planar configuration. The structure of the cesium salt is ionic. The structure of $\text{Ag}\{\text{ONC}(\text{CN})_2\}$ represents a 3D coordination polymer where the anion acts as tetradentate ligand with all 4 bonds between Ag(I) and donor atoms (3 N and 1 O) significantly shorter than the sum of the ionic radii for these elements. The silver(I) atom in this compound has a distorted tetrahedral surrounding. Additionally, $\text{Ag}\{\text{ONC}(\text{CN})_2\}$ is remarkably UV and visible light-insensitive. However, after exposure of solid complex to gases such as H_2 , CO, NO, C_2H_2 and C_2H_4 , surface of the compound becomes *visible light sensitive* and changes color with significant darkening which indicates reduction of the metal. This is reflected in a dramatic decrease of intensity of photoluminescence of $\text{Ag}\{\text{ONC}(\text{CN})_2\}$ in the presence of these gases which might be utilized for non-electric sensors applications. The $\text{Tl}\{\text{ONC}(\text{CN})_2\}$ complex represents a transitional species between ionic (Cs) and covalent (Ag) compounds. The thallium(I) center has four shorter than the sum of ionic radii bonds (3 with N and 1 with O atoms) and three longer, electrostatic (ionic) contacts with the anion. The $6s^2$ lone pair is stereo-active, and the coordination polyhedron is best described as a distorted square pyramid. Room temperature diffusion reflectance spectra of solid $\text{K}\{\text{ONC}(\text{CN})_2\}$, $\text{Ag}\{\text{ONC}(\text{CN})_2\}$ and $\text{Tl}\{\text{ONC}(\text{CN})_2\}$ demonstrated bathochromic shift of band's λ_{max} depending on the atomic number of the metal center indicating a significant role of metal centers in electronic transitions in these compounds. This phenomenon was observed for the first time. The latter complex at 293 K exhibited structured metal-based red photoluminescence in the range of 690 – 800 nm that depends on the excitation wavelengths.

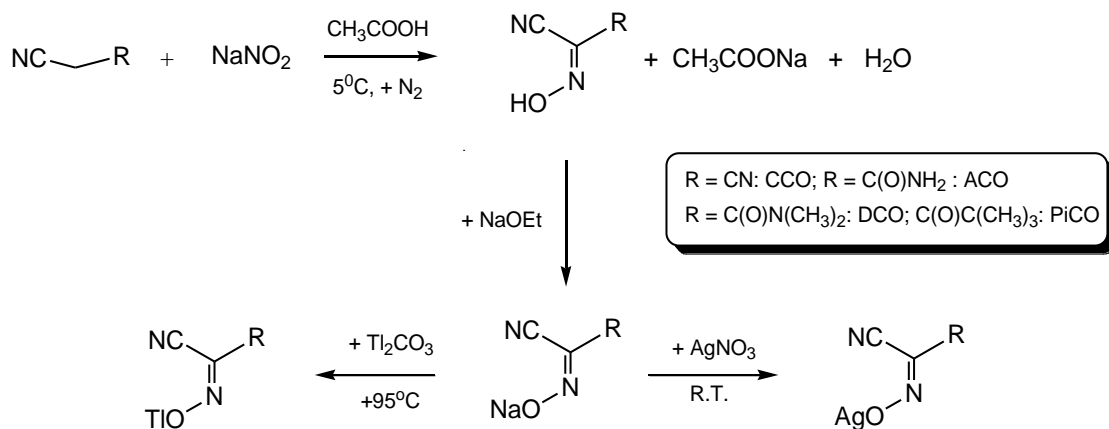


Figure 2. Typical route to cyanoxime ligands used in his work (A), and preparation of metal-containing compounds (B, C).

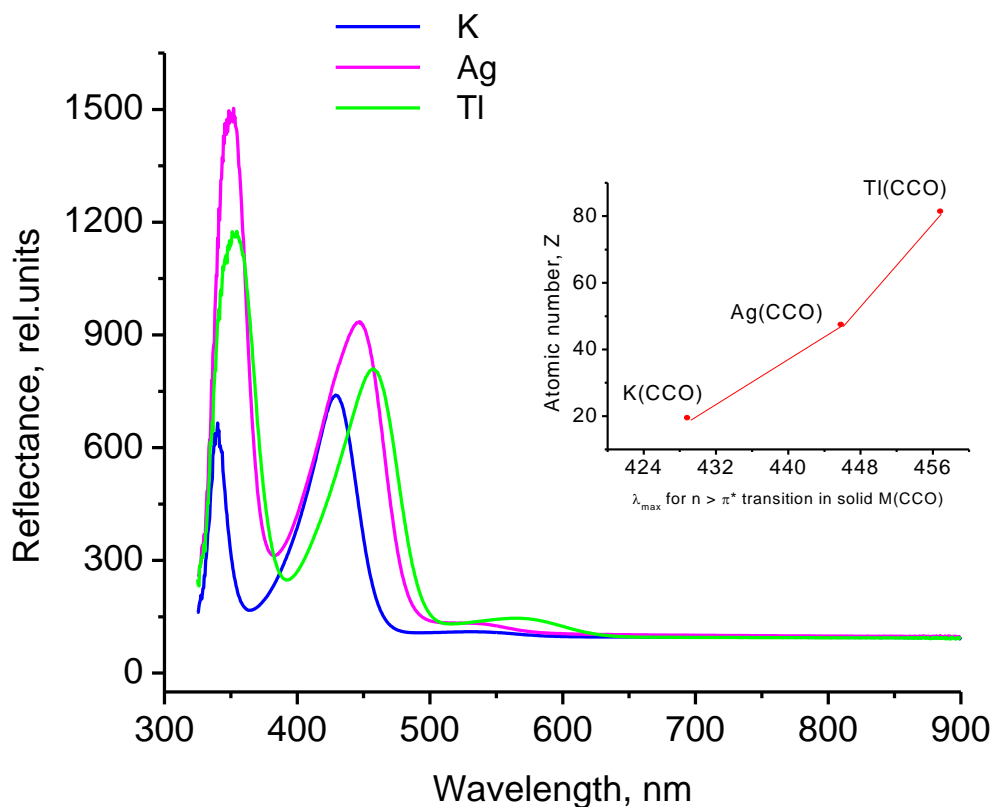
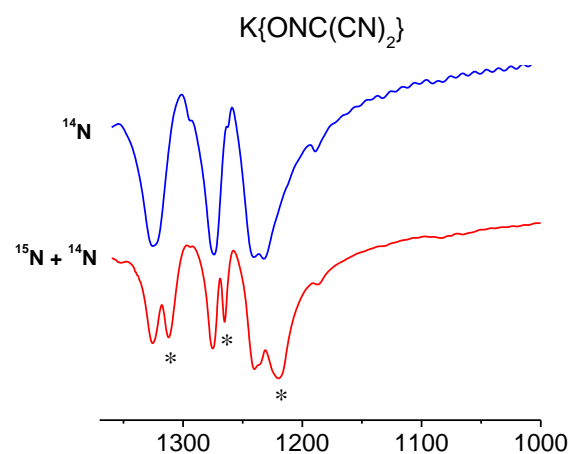
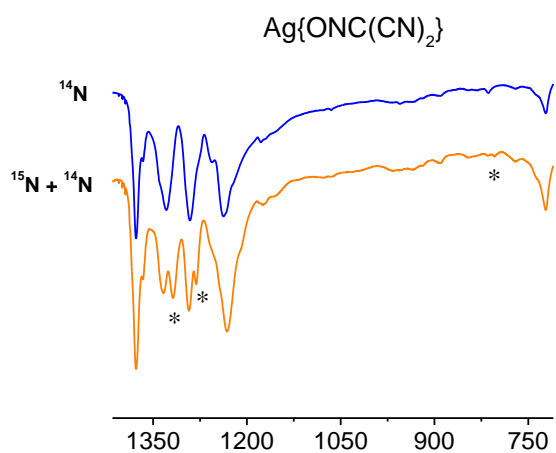


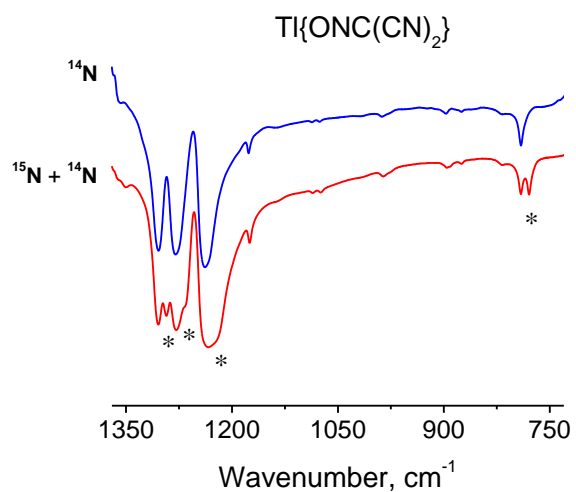
Figure 3. Diffusion reflectance spectra of $\text{M}\{\text{ONC}(\text{CN})_2\}$. An inset shows dependence of λ_{max} for the $n \rightarrow \pi^*$ intraligand transition upon the atomic number of the metal.



A



B



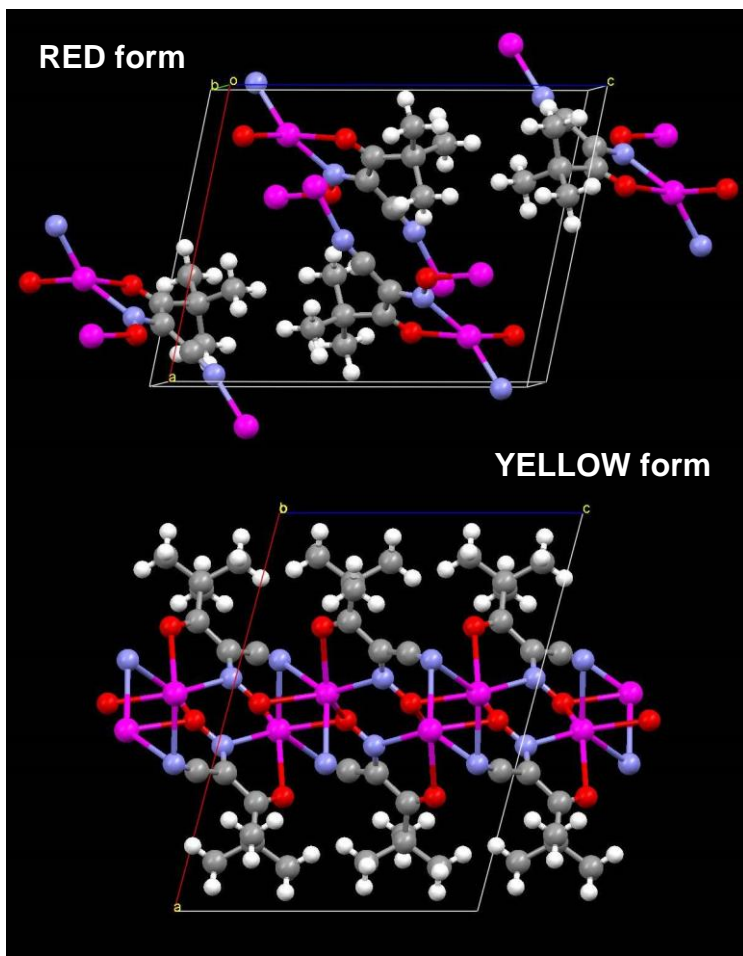
C

Figure 4. Overlaid fragments of the IR spectra of $\text{K}\{\text{ONC}(\text{CN})_2\}$ in KBr pellets (A), $\text{Ag}\{\text{ONC}(\text{CN})_2\}$ and $\text{Ti}\{\text{ONC}(\text{CN})_2\}$ in Nujol mulls (B, C). Asterisks indicate ^{15}N isotopomer bands.

During the last year of work in my research lab Garrett obtained one particular - Ag(PiCO) complex - which exists in two polymorph modifications: yellow and red (see Figure 5 below). They have different density, structure and photophysical properties. Garrett successfully grew crystals of both polymorphs suitable for X-ray analysis, and their structures were determined. Unit cells content for both polymorphs is shown side-by-side below.



A



B

Figure 5. A – photographs of two polymorphs of Ag(PiCO); B – unit cells comparative view.

Results of Garrets' work in my research laboratory are reflected in:

- 1) one major paper that was accepted in December of 2008 for publication in the ACS journal *Inorganic Chemistry*:

Glover, G.; Gerasimchuk, N.; Domasevitch, K.V. "Monovalent K, Cs, Tl and Ag Nitrosodicyanmethanides: Completely Different 3D Networks With Useful Properties." *Inorganic Chemistry*, **2008**, manuscript # ic-2208-1364w.R1

- 2) three presentations at the Midwest Regional ACS Meetings:

Gerasimchuk, N.; Domasevitch, K.V.; Glover, G.; Lewis, D.; Dalley, N.K.; Rath, N.P. "Silver(I) cyanoximates: synthesis, characterization and applications." Proceedings of 42nd Midwest Regional Meeting of the ACS, p.81; November 7-10th, 2007; Kansas City, MO.

Glover, G.; Gerasimchuk, N.; Domasevitch, K.V. "Heavy metals (M=Cs, Ag(I), Tl(I)) nitrosodicyanmethanides M[ONC(CN)₂]: synthesis, crystal structures and properties." Proceedings of 43rd Midwest Regional Meeting of the ACS, talk #49, p.64; October 8-11th, 2008; Kearney, NE.

Gerasimchuk, N.; Glover, G.; Gamian, A.; Domasevitch, K.V. "Further investigations of silver(I) cyanoximates". Proceedings of 43rd Midwest Regional Meeting of the ACS, talk #52, p.66; October 8-11th, 2008; Kearney, NE.



Graduation day! Garrett received his BS degree.



Garrett at the 21th Missouri Inorganic Day at University of Missouri Kansas-City.



Learning simple glassblowing technique.



Pictures in graduation day in front of two main pieces of equipment built with Garrett's help.





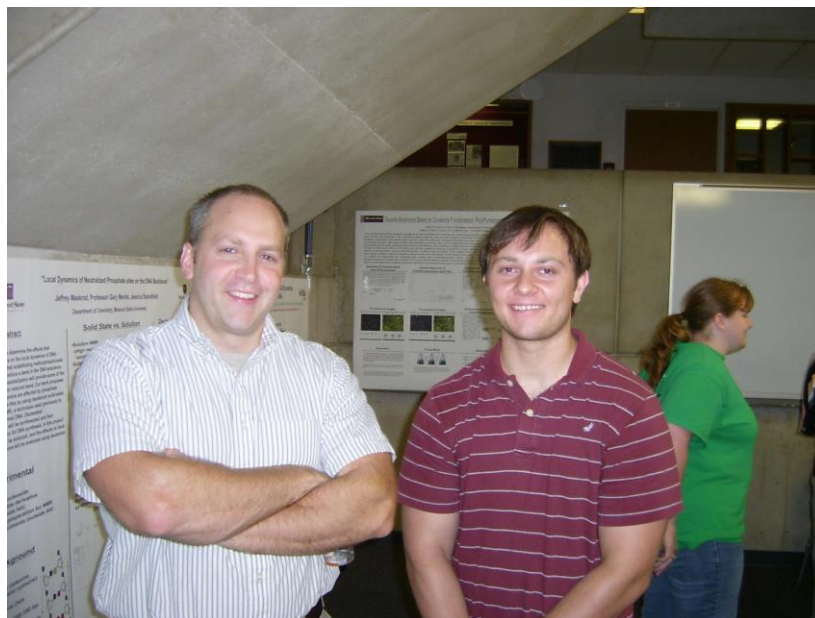
Midwest Regional ACS Meeting in Kearney, NE, October 2008



Trip to Nelson-Atkins Art Museum, Kansas City; spring 2007



Fun on Plaza (Kansas City, spring 2007)



During SURF exhibition/poster session; summer 2007