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 \( \pi-\pi \) 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.
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 CH$_3$-ONO, spectroscopically ($^1$H, $^{13}$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 (~95°C) aqueous solutions of Tl$_2$CO$_3$ and solid powdery monohalogenated arylcyanoximes HL. Crystal structures of two Tl(I) cyanoximates (Tl(2Cl-PhCO) and Tl(4Br-PhCO)) contained centrosymmetric dimeric units (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$_2$O$_2$ 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 Tl(I) salts are seen in Figure 4 below.

![Reaction Scheme](image)

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

**Figure 4.** Route to Tl(I) coordination polymers.
Figure 5. Molecular structures of several ligands used in his studies.

Figure 6. Actual photographs of long needles of Tl(2Cl-PhCO) at x 40 magnification.
Figure 7. Molecular structures of centrosymmetric dimers of Tl(2Cl-PhCO) (A) and Tl(4Br-PhCO) (B).

Figure 8. Capped-sticks view of structure of Tl(2Cl-PhCO) showing $\pi-\pi$ stacking stabilization of the lattice by 2-chloroaryl groups and close spatial location of metal ions (shown as van-der-Waals spheres; green).
Figure 9. Structure of coordination polymer in Tl(2Cl-PhCO). A – double ladder that consists of two slightly different Tl₂O₂ rhombs; B – details of rhombs geometry.

Figure 10. Capped-sticks view of structure of Tl(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 Br---Br interactions (olive color).
Figure 11. Structure of coordination polymer in Tl(4Br-PhCO). A – double ladder motif that consists of two slightly different Tl$_2$O$_2$ 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, Tl(I) and Ag(I) compounds.” Journal of Coordination Chemistry 2004, 57, No14, pp.1205-1216.

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


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.

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

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

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