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# Baumann Final Report:

## Structural Divergence of Heavy Metal Complexes with Isomeric Thiophenecarboxylates and Isotypic Selenophenecarboxylate

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The primary focus of my research has revolved around the structural divergence observed in the formation of metal-organic complexes when isomeric 2- and 3-thiophenecarboxylate (TCA) ligands are used. TCA's have emerged as exciting ligands highlighted in recent publications due to their interesting chemical structures and properties, yet it has remained relatively unexplored. TCA's interesting structure is composed of two components: the carboxylate group and the heterocyclic thiophene ring. The carboxylate group has been shown to readily bond to a variety of heavy metals across the periodic table in the P, D, and F blocks, as will be explained later. Additionally, the thiophene ring has been shown to harvest light well through its conjugated $\pi$-system. These two key properties have allowed TCA isomers to bond to different metals and enhance weak *f-f* LaPorte forbidden transitions of lanthanides. Lanthanides often present unique characteristics, such as second-generation harmonics or luminescence. Lanthanides are an underexplored area of the periodic table, so coupling research with TCA could lead to exciting new luminescent complexes.

The research project started with the continued exploration of a successful hydrothermal synthesis of 3-TCA and $Ho^{3+}$ by Grace Kuhl. 150 mM solution of 3-TCA in water was added to a PTFE autoclave liner and deprotonated with 6M NaOH. The nitrate salt was then dissolved into the solution. The liner was sealed in a stainless-steel autoclave and placed into a box furnace to be heated to 125°C for 12 hours (the time may be varied for other metals). The autoclave was then cooled at a rate of 5°C per hour. Once the reaction reached room temperature, the crystals were transferred to a petri dish. Crystals were cleaned and dispersed with 190-proof ethanol. Single crystals were manually isolated form the remaining matrix and run on a Rigaku SCX-mini Single Crystal X-Ray Diffractometer.

Figure 1. $[Ho(C_5H_3O_2S)_3(H_2O)_3][HC_5H_3O_2S]_3$

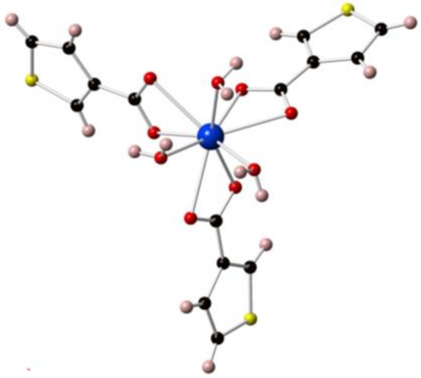

Figure 1. is shown here in its molecular structure bonded to three bidentate 3-TCA and three bound $H_2O$. This forms a nine-coordinate $Ho^{III}$ metal center with a principal C3 axis.

When the synthesis was repeated with 2-TCA, the resulting crystal structure was not isotypic to the 3-TCA structure. This interesting discovery opened the door to question why the two structures were divergent. We explored a variety of different nitrate salts to determine whether the structural divergence was unique to $Ho^{3+}$-TCA structures. With the exception of room temperature syntheses in alcohol solvents, every metal complex that yielded crystal structures with both 2-TCA and 3-TCA consistently showed divergence. This divergence was consistent across multiple oxidation numbers ($Ag^+$, $Pb^{2+}$, and $[Ln]^{3+}$).

Our leading theories suggested the following possibilities:

1. The size and of the sulfur atom results in unique crystal packing as it changes position.
2. The observed pKa difference between the two isomers suggests that the Lewis basicity is the driving factor of the structural divergence.

To resolve whether the size or pKa was the primary factor, 2-selenophenecarboxylate (2-SeCA) was chosen as an appropriate model candidate. 2-TCA and 2-SeCA have similar pKa values, but S and Se have different atomic radii. If size of the non-carbon atom is the primary factor in the crystal formation, then 2-SeCA crystal structures should diverge from 2-TCA crystal structures. If the pKa difference is the primary factor, then 2-SeCA and 2-TCA should show very similar crystal structures.

Table 1. Summary of Ligand pKa[1,2] and Atomic Radius Values

| | 2-SeCA | 2-TCA | 3-TCA |
|---|---|---|---|
| pKa | 3.43 | 3.49 | 4.08 |
| Group 16 Atomic Radius (pm) | 116 (Se) | 103 (S) | 103 (S) |

With the direction and help of Dr. Martin Hulce, 2-SeCA was synthesized through metalation of selenophene under inert $Ar_{(g)}$. Selenophene was cooled to -70°C in a round-bottom flask. N-butyllithium was added to the round-bottom flask dropwise via cannula in slight excess. N-butyllithium has the potential to combust, so the inert gas was a safety requirement. It was allowed to react for 30 minutes before the solution was brought up to 0°C for 5 minutes. The product was poured over crushed dry ice and brought up to room temperature. 50mL of $H_2O$ were added to the solution along with concentrated sulfuric acid. The acid was then extracted into ether and dried. Two products formed: a dark sludge and clear crystals. A qualitative solubility test showed that the clear crystals were soluble in water while the dark sludge was not. Therefore, the product was recrystallized in warm water with the dark sludge being filtered off. X-Ray Diffraction verified that the crystals obtained were 2-SeCA.

With the 2-SeCA successfully synthesized, we could now attempt to form heavy metal crystal structures. Using the same hydrothermal method as reactions with 2-TCA, a $Pr^{3+}$/2-SeCA crystal structure was found to be isotypic to the $Pr^{3+}$/2-TCA structure previously observed in the project. This 2-SeCA crystal, the first 2-SeCA crystal ever solved, supports the theory of pKa as the primary factor for the structural divergence. In total, 25 novel compounds have been discovered through this research.

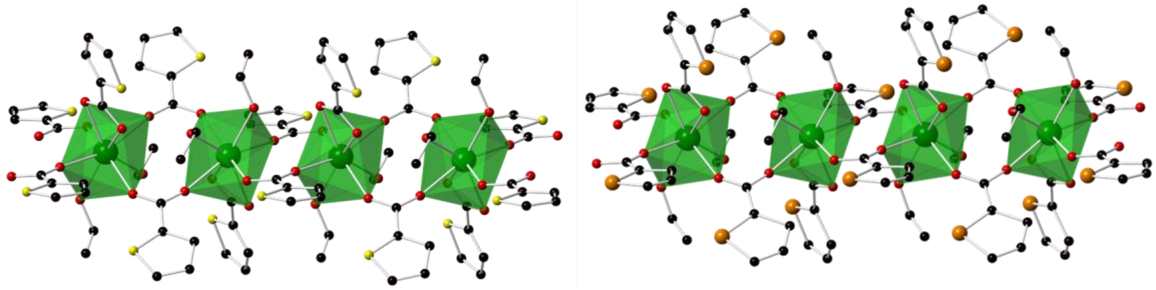

Figure 2. Pr3+ with 2-TCA(left) or 2-SeCA(right) at room temperature conditions in EtOH. These crystals were shown through XRD to be isomorphic, but they're structural continuity can be visually observed.

1. **Experimental and Computational Thermochemistry of 2- and 3-Thiophenecarboxylic Acids**
   Manuel Temprado,Maria Victoria Roux,*, Pilar Jiménez,Juan Z. Dávalos, and, and Rafael Notario*
   *The Journal of Physical Chemistry A* **2002** *106* (46), 11173-11180
   DOI: 10.1021/jp020896p

2. **Thermodynamics of Protonation of Some Five-membered Heteroaryl-carboxylates, alkanoates and -*trans*-propenoates**
   Giuseppe Arena, Rosario Cali, Emanuele Maccarone and Amedeo Passerini. *Journal of the Chemical Society, Perkin Transactions* **1993** *2*, 1941-1945.