

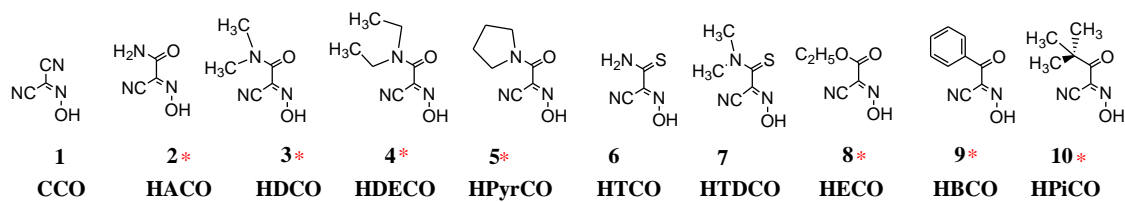


Adedamola Abraham Opalade: MS 2016

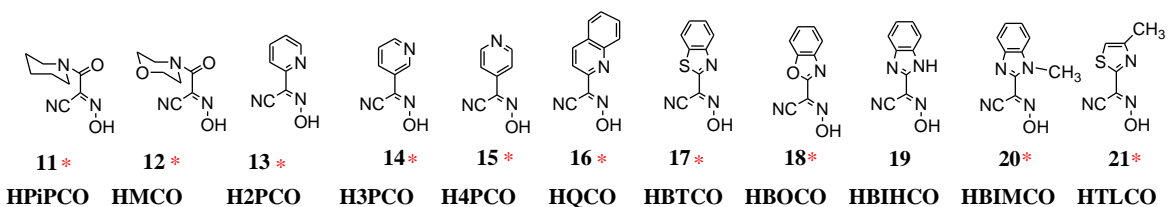
**Thesis “THE SYNTHESIS AND CHARACTERIZATION OF Ni(II)
AND Cu(II) CYANOXIMATES”**

Abraham Opalade was a graduate MS student from Nigeria. He approached me in early Fall semester of 2014 and expressed desire to work in my laboratory on a research project of my choice. Since he already showed a very good performance in classes of my inorganic chemistry curriculum at Missouri State University, I accepted him as a MS degree candidate. During 2,5 years of work until his thesis defense in April of 2016 he completed truly phenomenal amount of work and showed the greatest degree of motivation and perseverance I have ever seen in my academic career at MSU.

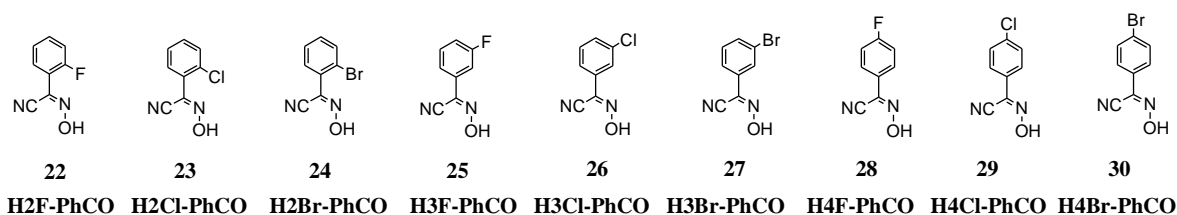
In the nutshell, I have assigned to Abraham the research project that was intended to be a “clean-up” work in the area of commonly used transition metals – Cu, Ni – and their coordination compounds with chelating cyanoximes. Well, as it frequently turns out, the project upon carrying out of some work and gaining first results appeared to be much more deep and interesting than originally anticipated. At first, the list of all currently known cyanoxime ligands is presented in Figure 1. Several of those ligands have strong propensity for the formation of chelating rings with metal ions. In my previous investigations we did use some of them, but the whole work was very patchy.



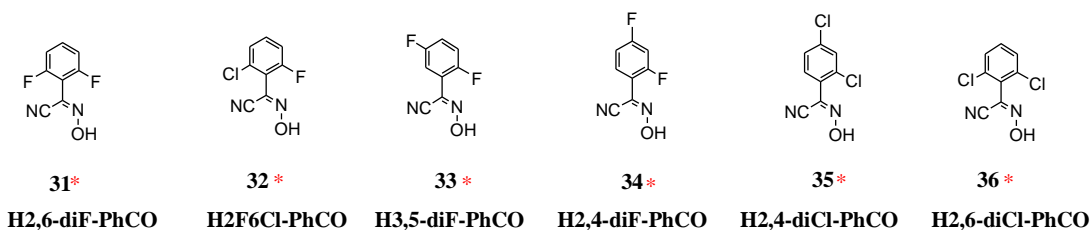
Amido- / ester- and keto- cyanoximes



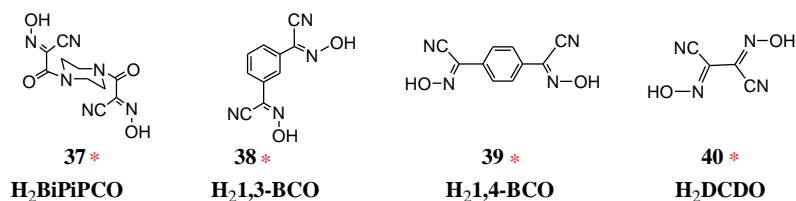
Heterocyclic cyanoximes



Monosubstituted arylcyanoximes



Disubstituted arylcyanoximes



Bis-cyanoximes

Figure 1. The list of cyanoxime ligands. * - Crystal structures were determined.

Thus, Abraham received the task to prepare coordination compounds with set chelating ligands shown in Figure 2 that either were never prepared at all, or were poorly studied. Metals were selected to be of *3d* series: bivalent Ni and Cu.

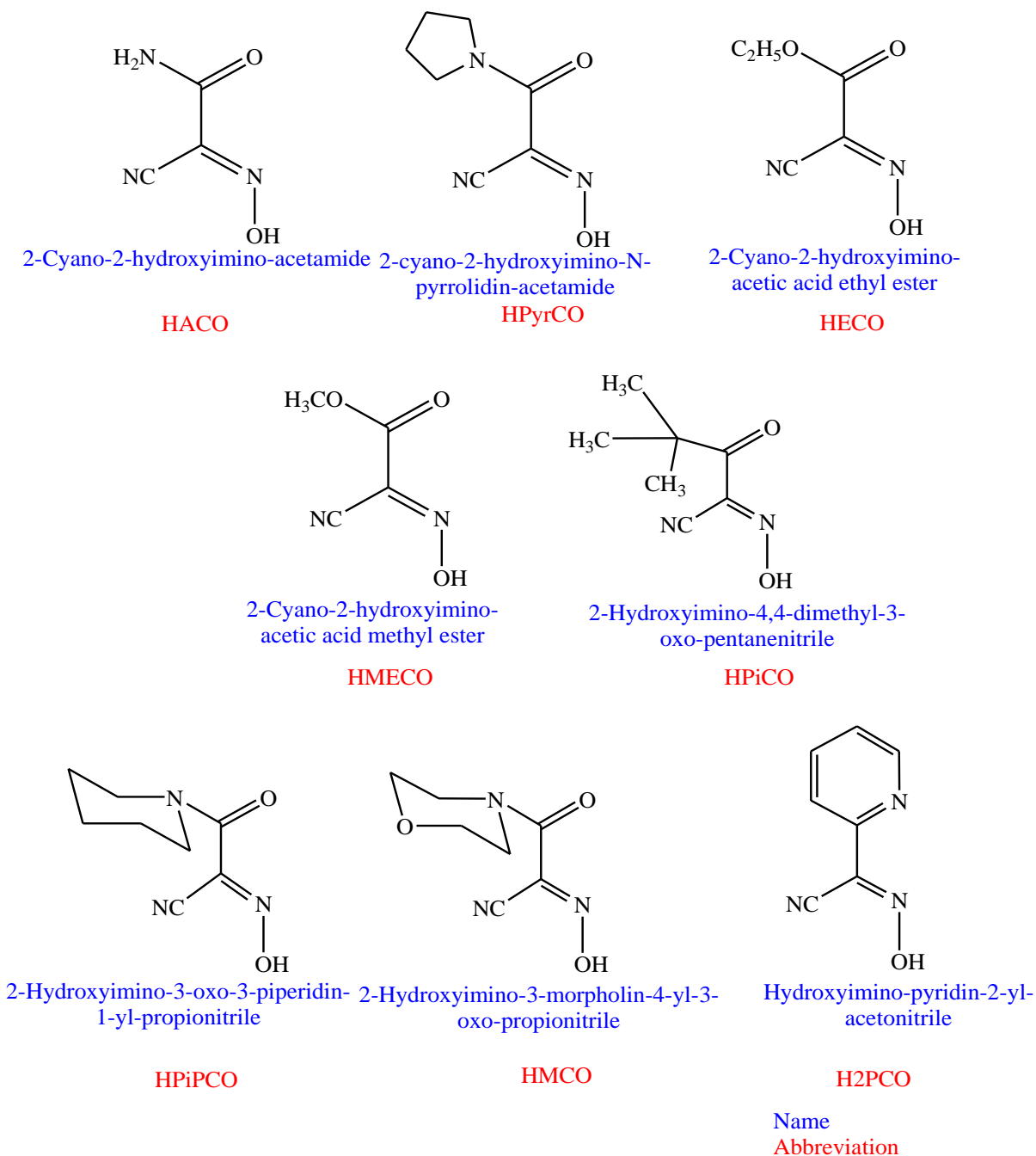


Figure 2. Cyanoxime ligands used for our studies accompanied with their abbreviations.

MS thesis ABSTRACT

Metal complexes of hydrated Cu(II) and Ni(II) with several cyanoximates were synthesized and characterized by elemental analysis, thermal analysis, IR-, electronic- (solid state diffuse reflectance) spectroscopy, and the X-ray analysis (powder diffraction and single crystal studies). Hydrolysis of the HECO and HMeCO cyanoxime ligands leads to the formation of another dianionic cyanoxime – AACO^{2-} , which forms multimetallic Cu(II) and Ni(II) complexes and oxamide as a side product. The crystal and molecular structures of 8 compounds were determined (6 metal complexes and 2 organic compounds). Two Ni metal complexes have distorted octahedral structures with the cyanoximes acting as a chelating ligand, one Cu metal complex has distorted square pyramidal structure and three metal complexes of Cu and Ni were found to be multimetallic with two different environments: penta- and hexa-coordinated which correspond to distorted square pyramidal and octahedral geometries. The trimetallic complexes of Ni(II) and Cu(II) with AACO^{2-} are isostructural. The tri-copper(II) complex demonstrates significant antiferromagnetic interactions between the cyanoxime-bridged metal centers at room temperature. All metal complexes have both coordinated, and crystallization water molecules, which are essential for the crystal packing via the system of H-bonds. The hydrated complexes of Ni(II) of selected cyanoximes were dehydrated, and respective anhydrous complexes were obtained and characterized. Electronic spectroscopy and XRD powder diffraction studies of the anhydrous complexes evidenced the retention of geometry of the central Ni atom after dehydration which suggests bridging function of cyanoximes in the lattices even after water loss. Rehydration of the anhydrous complexes were performed and three of the complexes showed reversible hydration-dehydration reactions.

KEYWORDS: cyanoximes, Ni(II) and Cu(II) complexes, crystallohydrates, TG/DSC, IR- and UV-Visible spectroscopy, X-ray single crystal analysis, XRD powder diffraction, magneticsm.

RESEARCH GOALS

Literature review revealed that there were some studies of Cu(II) and Ni(II) complexes with several cyanoximes in the past. However, no significant comparative investigation of these metal ions with a series of chelating cyanoximes has been done. Also, it was unknown what happens to the hydrated Cu and Ni cyanoximes upon H_2O removal. Thus the goals of current research project were:

1. To synthesize series of Ni(II) complexes with chelating cyanoxime ligands as hydrates and their anhydrous complexes, investigate structural rearrangement in the complexes upon dehydration (Figure 3) and perform oxidation of the anhydrous Ni-complex in order to form mixed valence system as shown in Figure 4.
2. Prepare, characterize and study a series of analogous Cu(II) cyanoximates and compare them with Ni(II) complexes in a hope that the application of the EPR spectroscopy and magnetochemistry will allow such comparison.

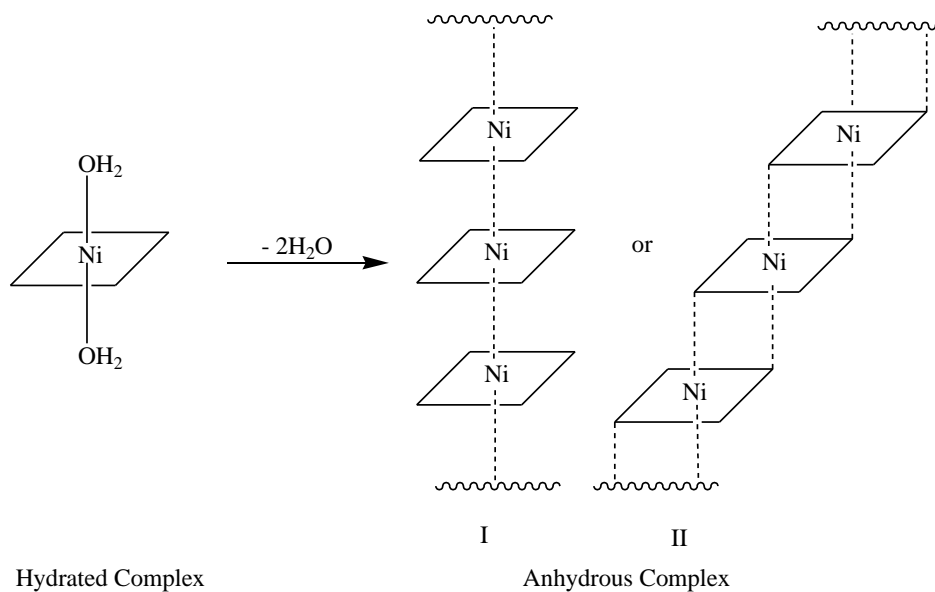
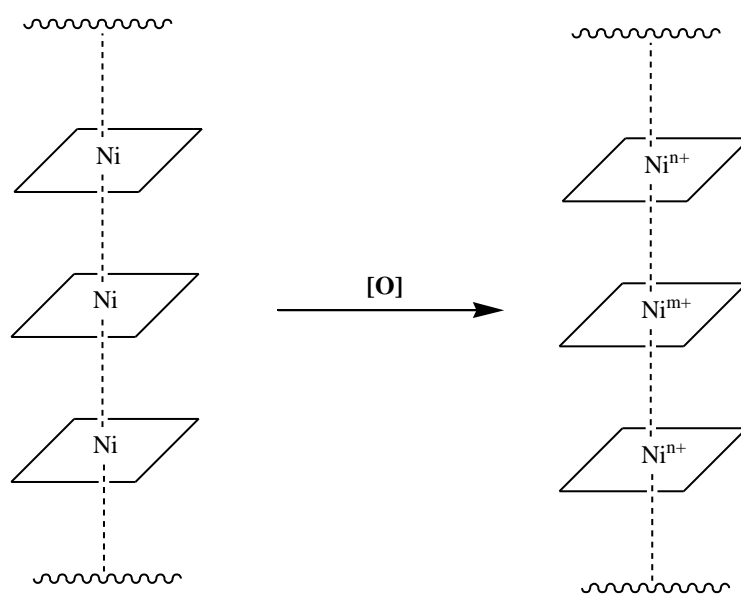


Figure 3. Possible structural rearrangement after dehydration of Ni(II) complexes with chelating cyanoximes.



$n+ = +2$ oxidation state and $m+ = +3$ or $+4$ oxidation state

Figure 4. Oxidation of anhydrous complex with direct Ni----Ni interaction to create a mixed valent Ni-system.

RESULTS:

General methods of making listed below coordination compounds together with their actual appearance are shown in Figure 5 – 14 below.

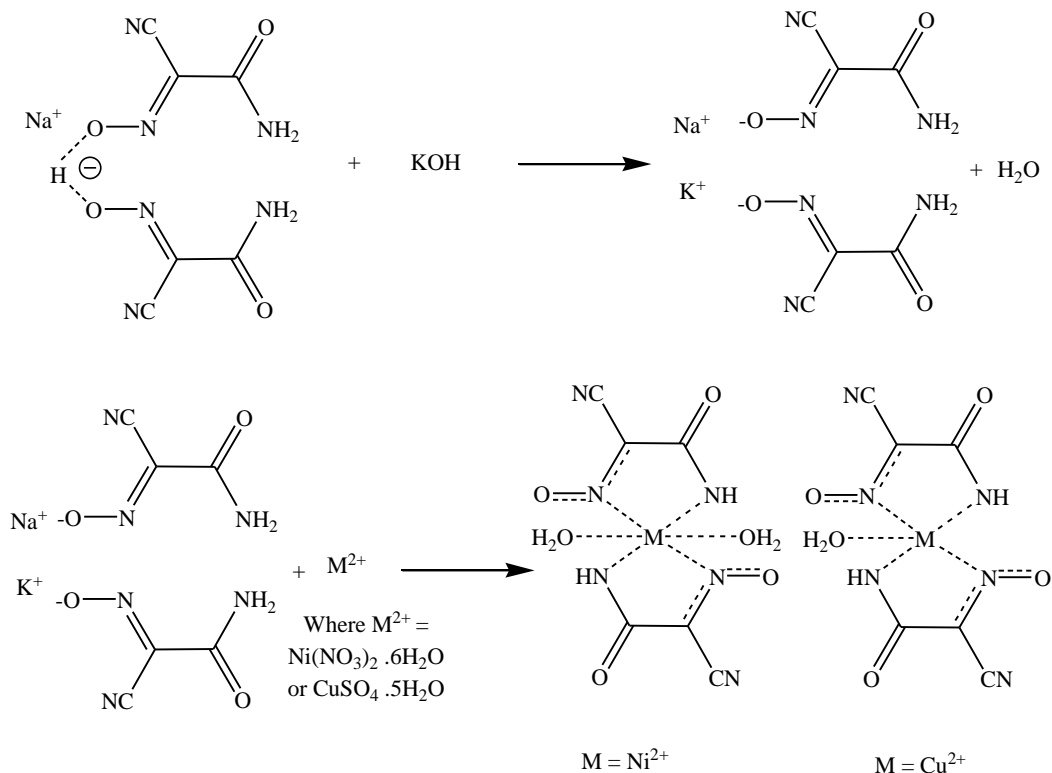


Figure 5. Scheme of syntheses of Ni (II) and Cu(II) complexes of the HACO ligand.

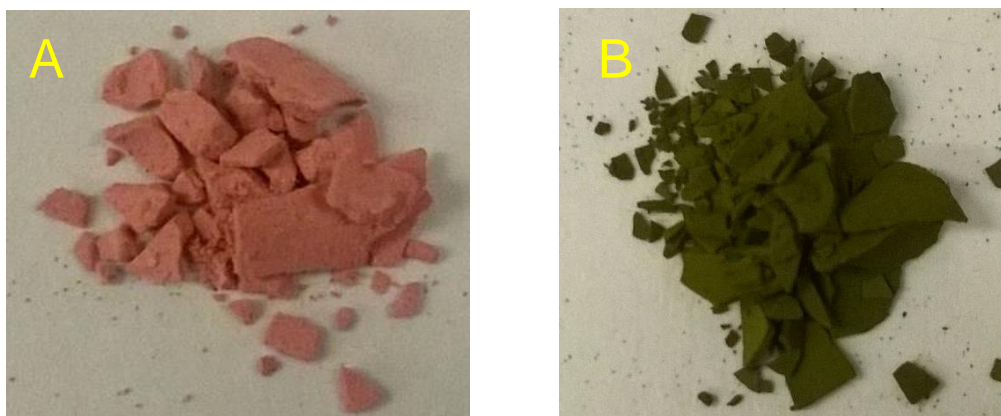


Figure 6. Bulk precipitates of the $[\text{Ni}(\text{ACO})_2 \cdot 2\text{H}_2\text{O}]$ (A) and $[\text{Cu}(\text{ACO})_2 \cdot \text{H}_2\text{O}]$ (B) Complexes. Photograph taken using Motic Microscope at 40x magnification.

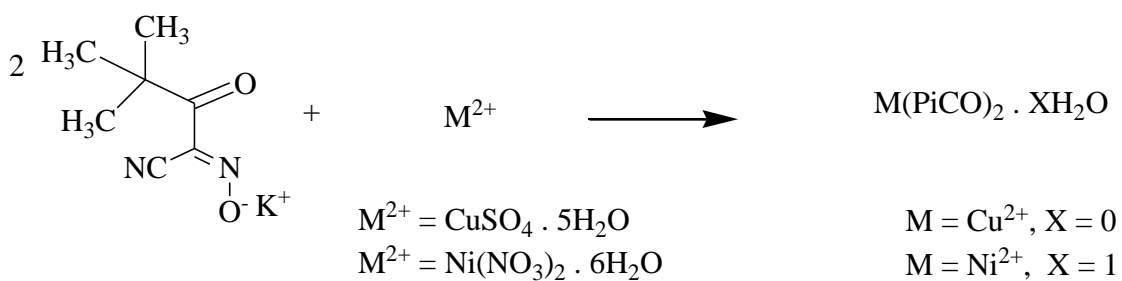
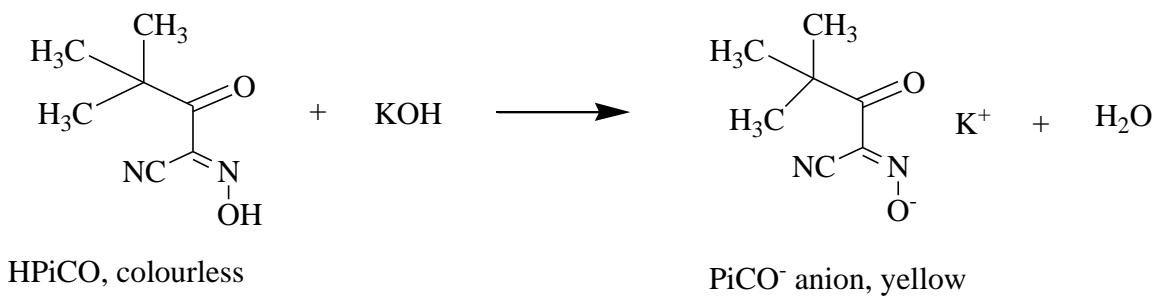


Figure 7. Syntheses of Ni(PiCO)₂·H₂O and Cu(PiCO)₂.



Figure 8. Microscope photographs of bulk precipitate of Ni(PiCO)₂·H₂O (A) and Cu(PiCO)₂ (B) obtained at 40x magnification.

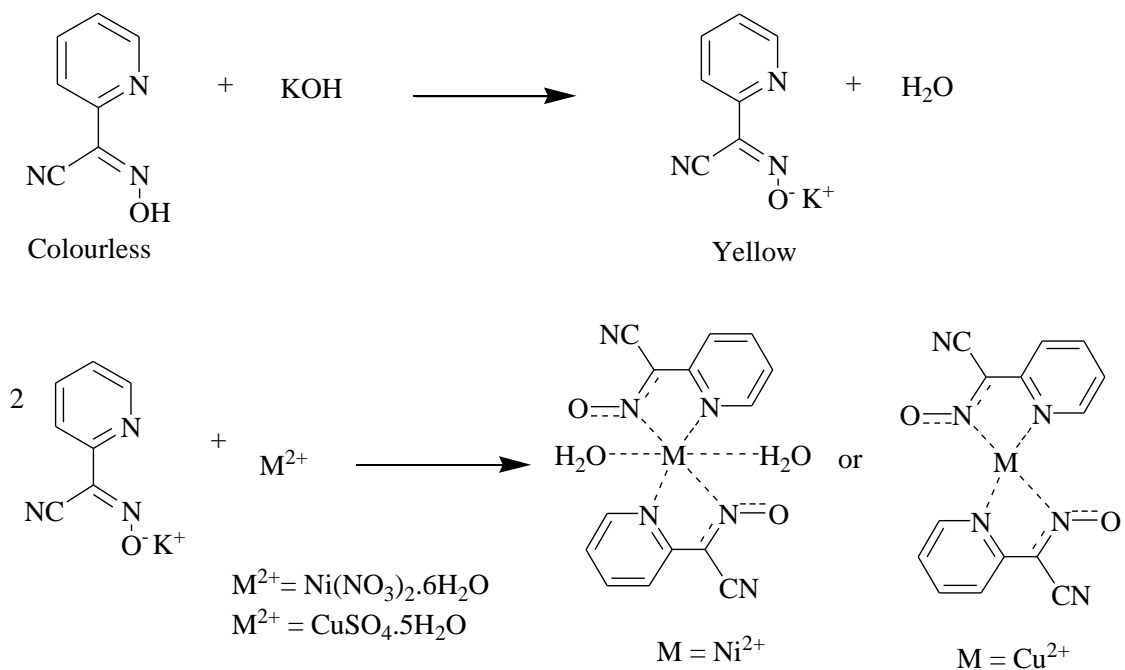


Figure 9. Preparation of Ni(II) and Cu(II) complex of H(2PCO) cyanoxime.



Figure 10. Actual microscope photographs of bulk precipitate of [Ni(2PCO)₂·2H₂O] (A) and Cu(2PCO)₂ (B) at x40 magnification.

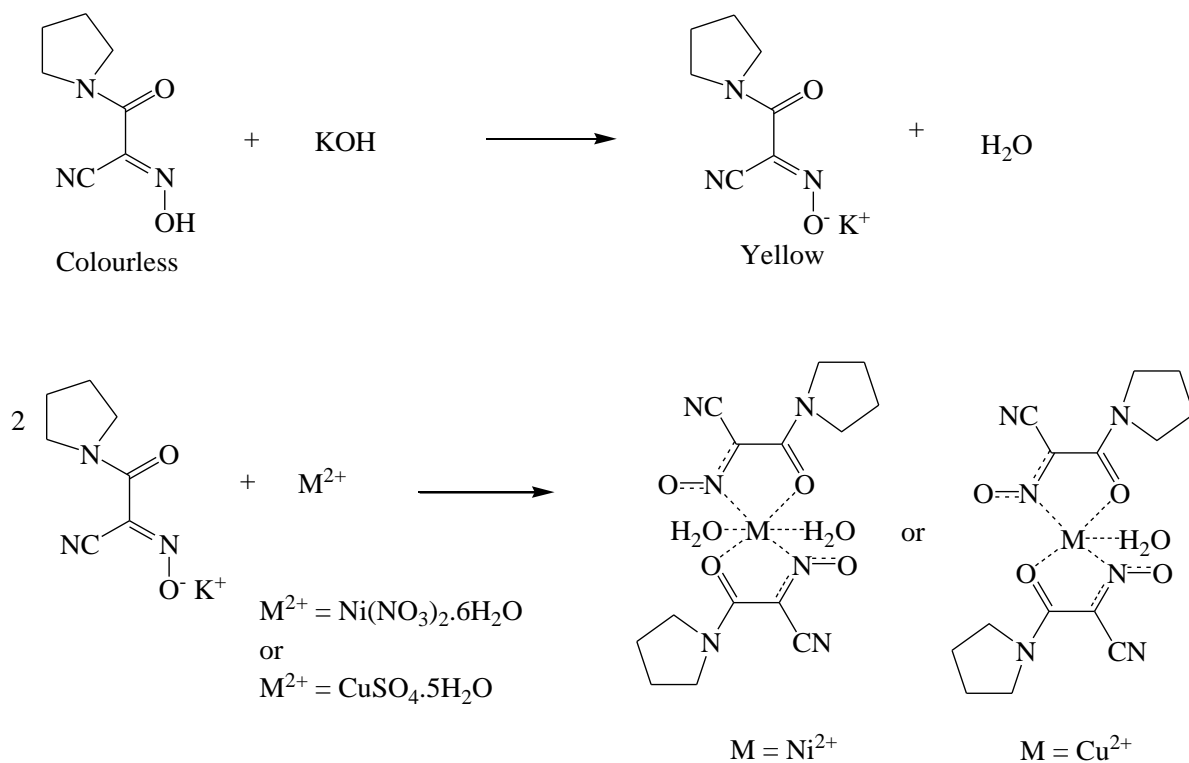


Figure 11. Syntheses of Ni(PyrCO)₂·2H₂O and Cu(PyrCO)₂·H₂O.



Figure 12. Microscope photographs of bulk Precipitate of Ni(PyrCO)₂·2H₂O (A) and Cu(PyrCO)₂·H₂O (B) at x40 magnification.

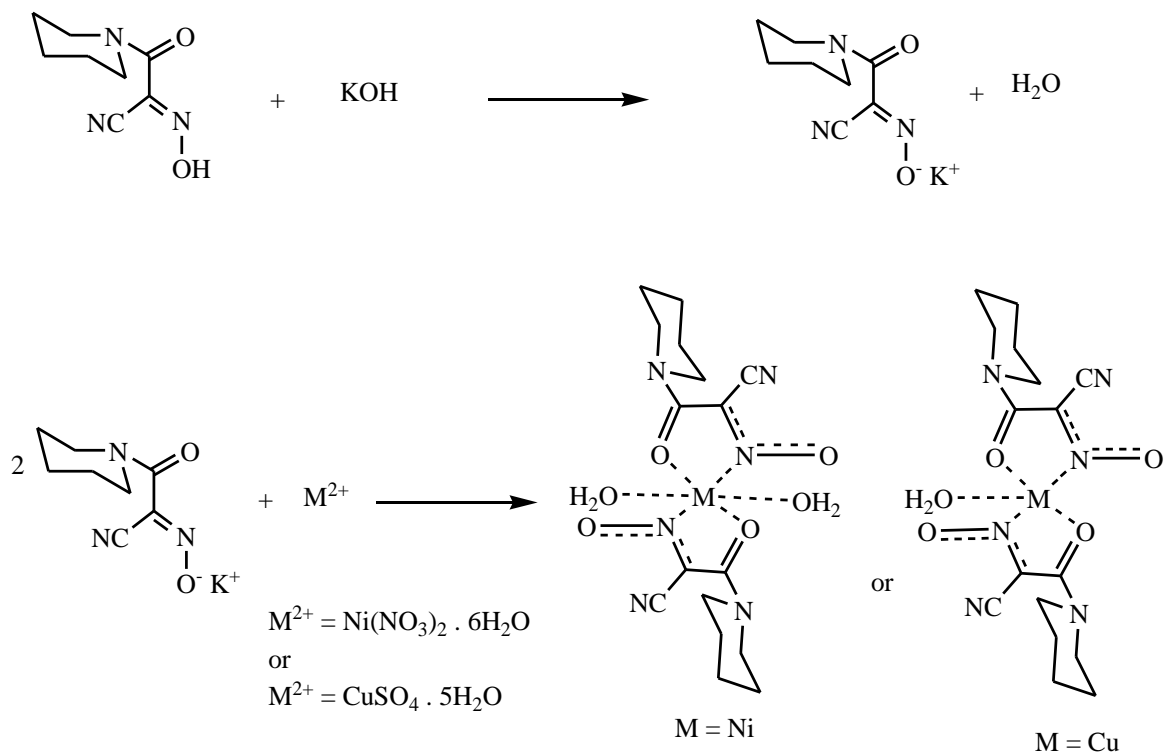


Figure 13. Syntheses of the Ni (II) and Cu(II) complexes of HPiPCO cyanoxime.



Figure 14. Microscope photographs of bulk precipitate of Ni(PiPCO)₂·2H₂O (A) and Cu(PiPCO)₂·H₂O (B), taken at x40 magnification.

It was possible to crystallize some of the metal complexes as well as a new polymorph of one of the cyanoxime carboxylic esters used – HECO. Crystal data for these complexes are presented in Figures 15 – 18.

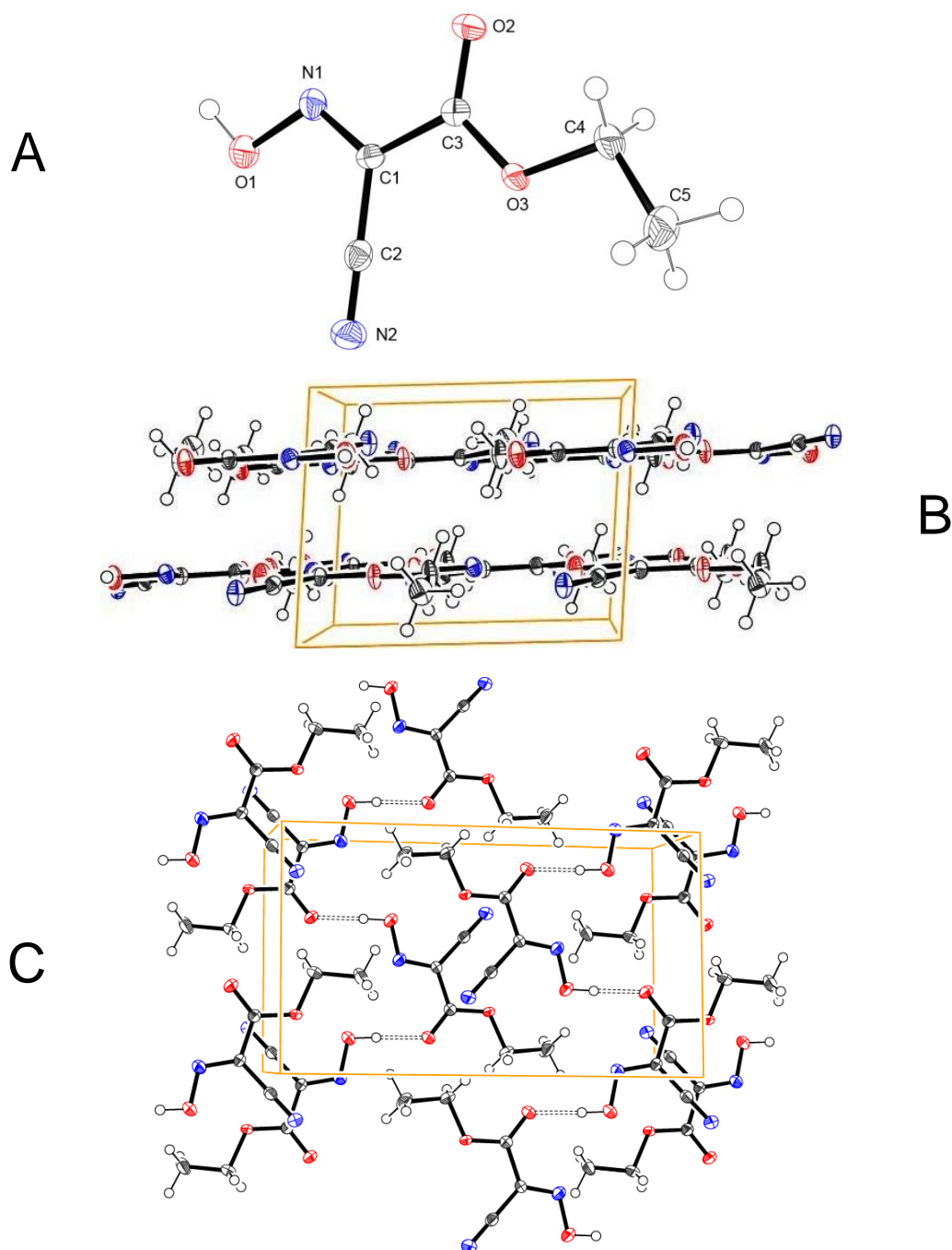


Figure 15. Structure of low temperature polymorph of the HECO. A – molecular structure and numbering, B – unit cell content showing layered crystal packing, C - H-bonding between molecules inside the layer in the structure of cyanoxime.

Crystal data: T = 120 K; in P21/c; GOF = 1.146; R1 = 5.45%

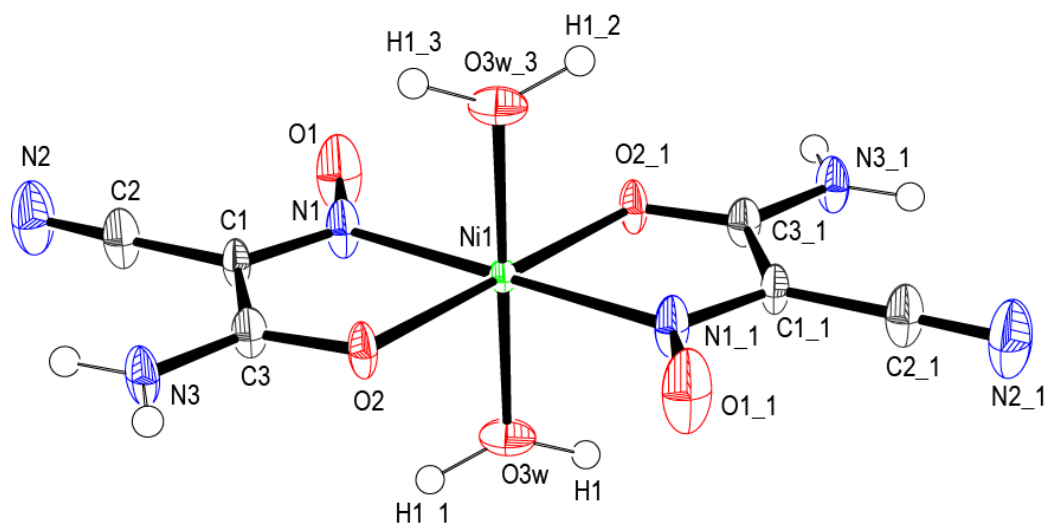


Figure 16. The GROW fragment in the structure of $[\text{Ni}(\text{ACO})_2 \cdot 2\text{H}_2\text{O}]$. Symmetry codes for 1: $x, -y, -z$; for 2: $-x, y, z$; for 3: $-x, -y, -z$.

Crystal data: $T = 120 \text{ K}$; in Cmca ; $\text{GOF} = 1.041$; $R1 = 4.17\%$

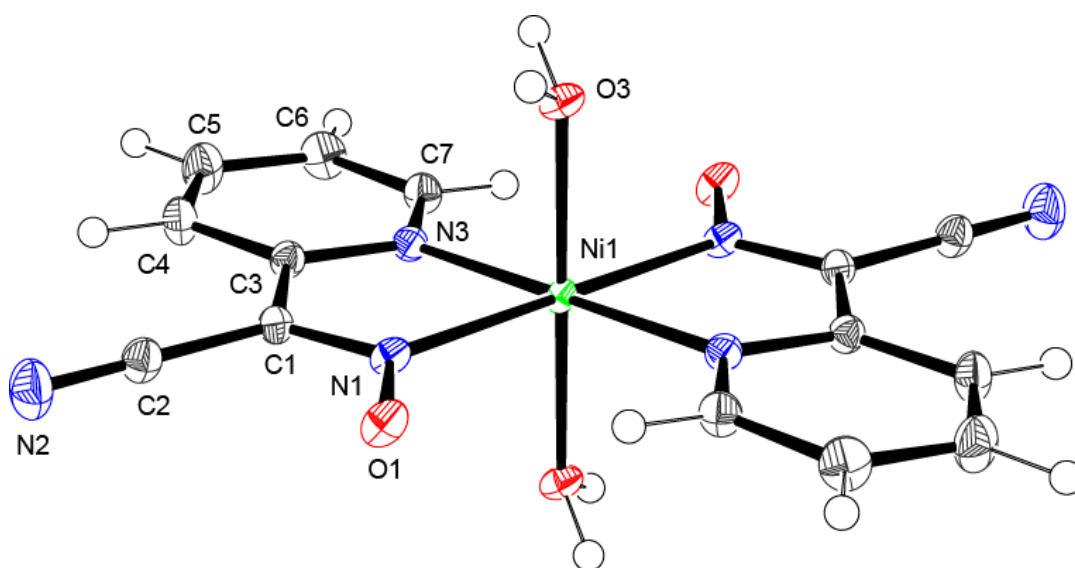


Figure 17. Molecular structure and numbering scheme for $[\text{Ni}(\text{2PCO})_2 \cdot 2\text{H}_2\text{O}]$.

Crystal data: $T = 120 \text{ K}$; in P-1 ; $\text{GOF} = 1.043$; $R1 = 3.24\%$

Abraham found that two of ester-cyanoxime ligands HECO and HMeCO hydrolyze at experimental conditions to form cyanoxime-carboxylic acid HAACO and its dianion. Being polyfunctional double-charged ion, the AACO^{2-} forms very interesting polymetallic (polynuclear) complexes structures of which are presented below in Figures 18-23.

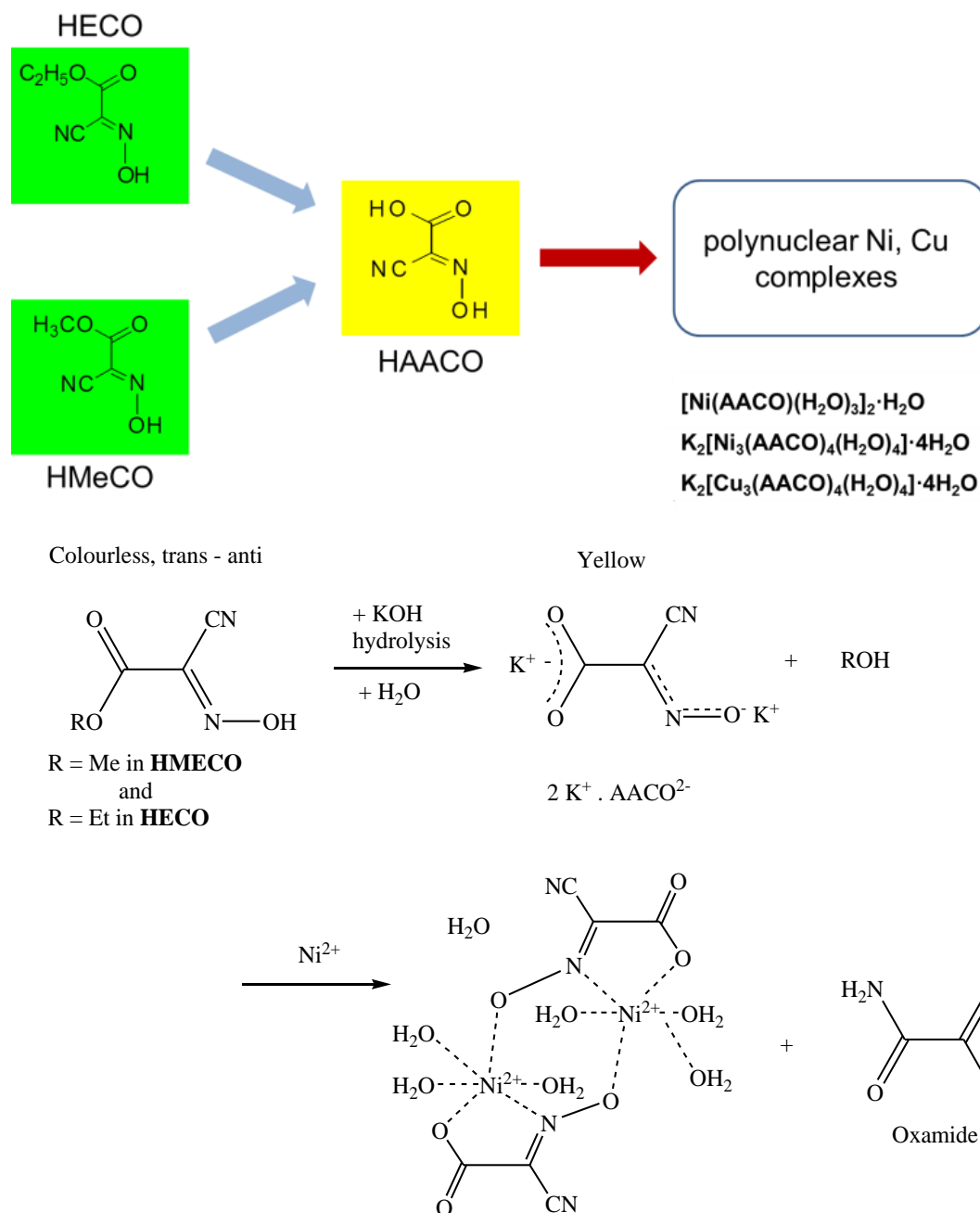


Figure 18. Formation of the AACO^{2-} metal complex via hydrolysis of ester fragment.

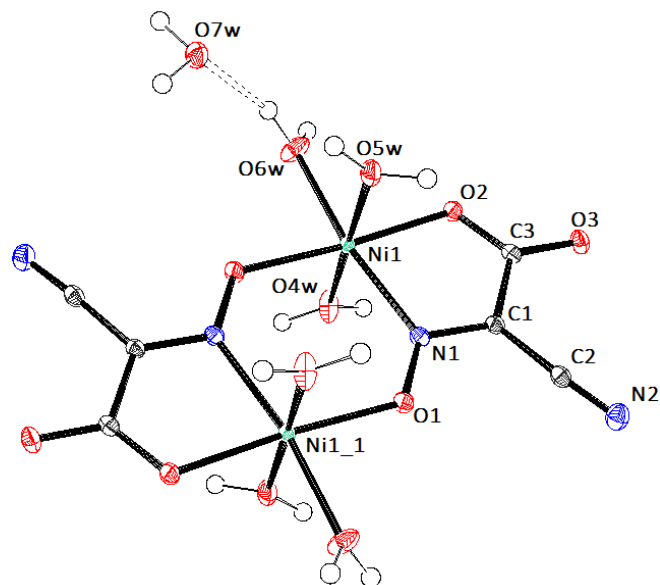


Figure 19. The GROW fragment in the dimetallic structure of $[\text{Ni}(\text{AACO})\cdot(\text{H}_2\text{O})_3]_2\cdot\text{H}_2\text{O}$. The inversion center is located half-way between two Ni atoms. The symmetry operation for the $_{-1}$ code is $-x, y, -z+1/2$.

Crystal data: T = 120 K; in $C2/c$; GOF = 1.147; R1 = 2.69%

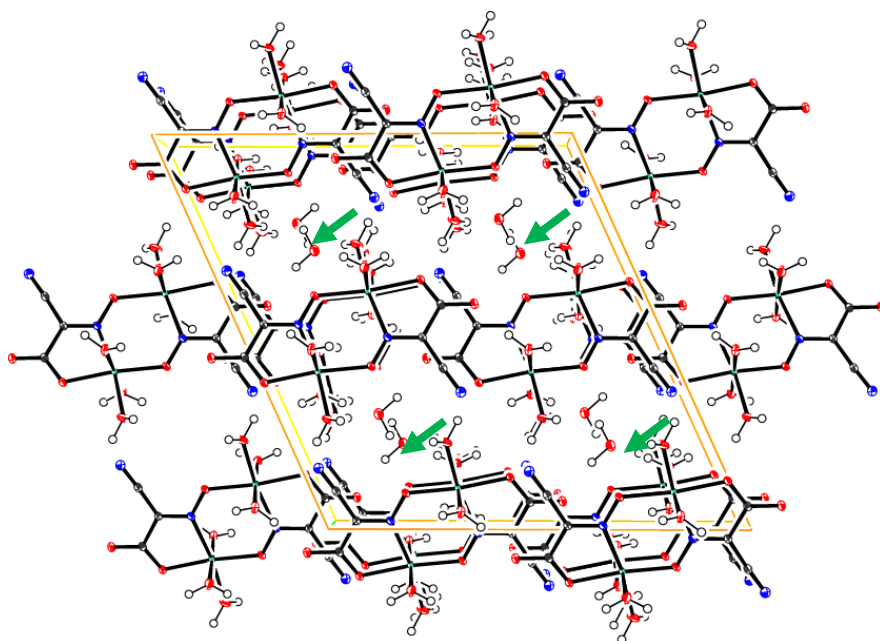


Figure 20. The unit cell content in the structure of $[\text{Ni}(\text{AACO})\cdot(\text{H}_2\text{O})_3]_2\cdot\text{H}_2\text{O}$: view normal to $[010]$ plane. Green arrows indicate water molecules occupying channels running along b -direction.

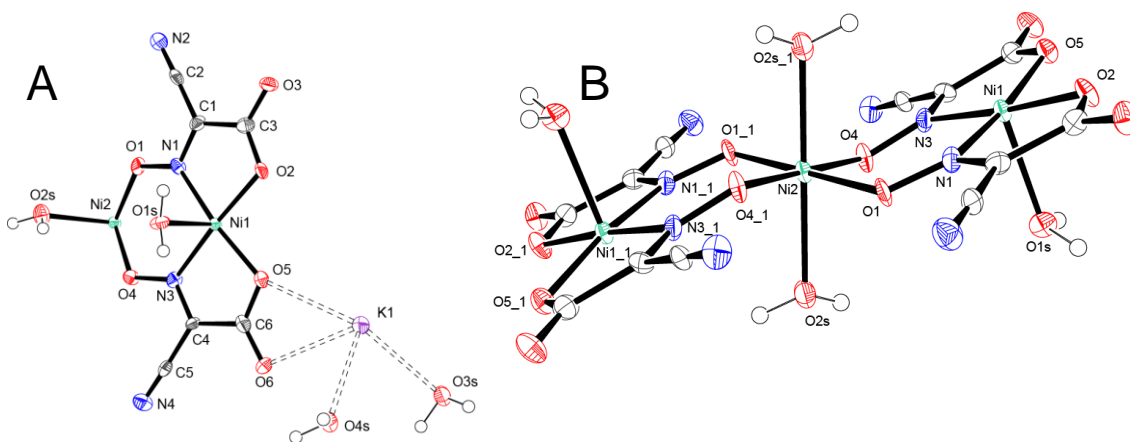


Figure 21. A - Asymmetric unit of $K_2[Ni_3(AACO)_4(H_2O)_4] \cdot 4H_2O$ showing the numbering scheme; long electrostatic contacts with alkali metal cation are shown as dashed lines. B - Structure of the $[Ni_3(AACO)_4(H_2O)_4]^{2-}$ dianion with K^+ counter ions and associated water molecules being omitted for clarity.

Crystal data: T = 273 K; in $P2_1/n$; GOF = 1.045; R1 = 4.80%

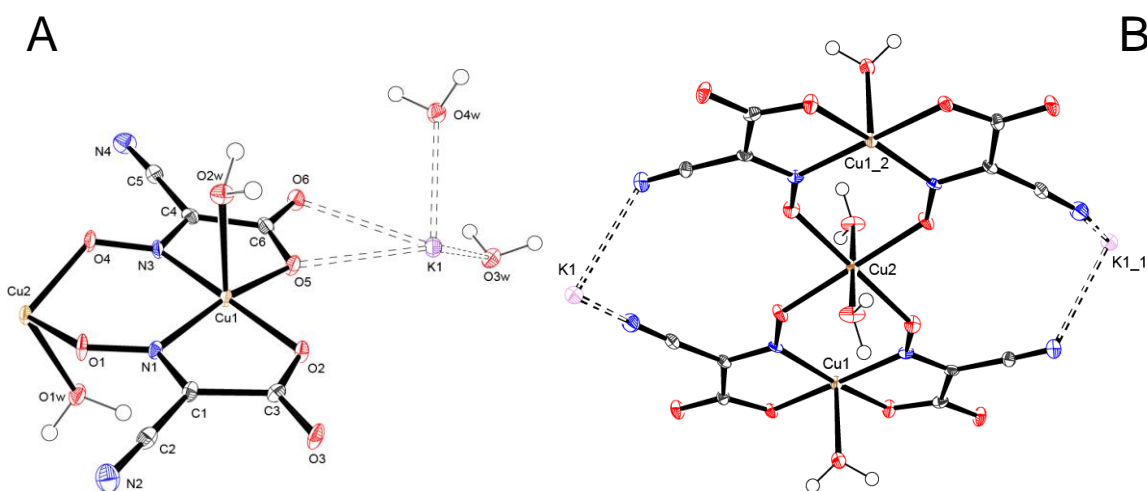


Figure 22. A - The asymmetric unit in $K_2[Cu_3(AACO)_4(H_2O)_4] \cdot 4H_2O$, showing the atomic numbering scheme. B - Coordination around the Cu2 atom in the structure, showing the connectivity of potassium counter ions to the $[Cu_3(AACO)_4(H_2O)_4]^{2-}$ dianion; long electrostatic contacts around K^+ are indicated as dashed lines.

Crystal data: T = 120 K; in $P2_1/n$; GOF = 1.025; R1 = 4.26%

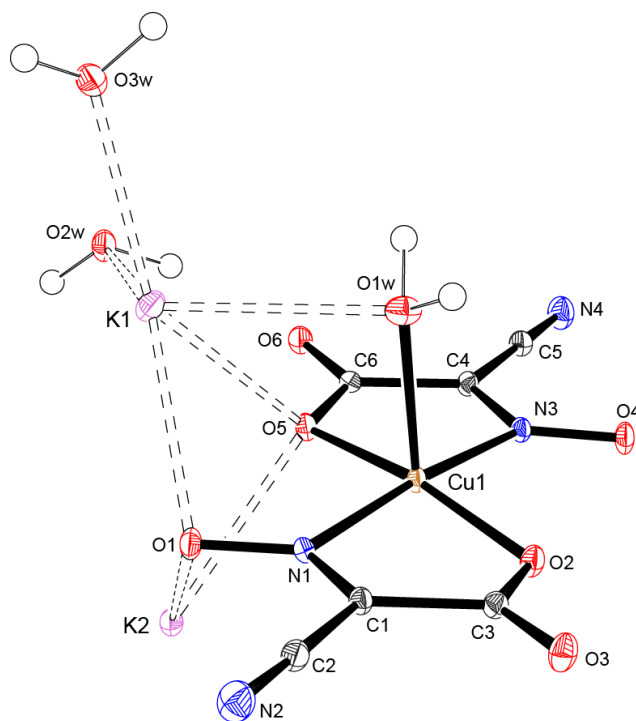


Figure 23. The ASU in the structure of $K_2[Cu(AACO)_2 \cdot H_2O] \cdot 2H_2O$ (4). Clearly shown is the *trans*-geometry of the chelating $AACO^{2-}$ anion in the complex. Dotted lines show electrostatic contacts.

Crystal data: T = 100 K; in $P2_1/c$; GOF = 1.002; R1 = 2.42%

SUMMARY AND CONCLUSION from Abraham Opalade's work:

- As the result of this study we obtained 23 compounds: 3 organic and 20 metal complexes of bivalent Cu (7) and Ni (13). Two organic ligands – HECO and HMCO – were known before and prepared in the research group, while the oxamide, $C_2N_2O_2H_4$, was obtained as a side product. Our goal of preparation of a series of transition metal cyanoximates was accomplished, albeit not to the desired level. The main obstacle was a hydrolysis reaction of the ether-cyanoximates HECO and HMeCO that lead to the formation of another cyanoxime – $AACO^{2-}$ dianion $C_3N_2O_3^{2-}$, which formed elegant dimeric and trimeric complexes with Cu(II) and Ni(II).
- Synthesized metal complexes were characterized by elemental analysis, thermal analysis, IR and electronic (solid state, diffuse reflectance) spectroscopies and X-ray analysis. The latter technique included both powder diffraction, and single

diffraction studies. Thus, crystal and molecular structures of 8 complexes were determined: 6 for transition metal complexes and 2 for organic compounds – HECO cyanoxime and side product such as oxamide. The origin of appearance of this compound is postulated.

- Two metal complexes – $[\text{Ni}(\text{ACO})_2(\text{H}_2\text{O})_2]$ and $[\text{Ni}(\text{2PCO})_2(\text{H}_2\text{O})_2]$ – form molecular, island type structures with rhombically distorted octahedral Ni(II) environment. In both complexes the cyanoximes act as chelating ligands, adopt *cis-anti*, *nitroso-* structures and form complexes with *cis*-geometry of mutually oriented anions in equatorial plane. Water molecules occupy axial positions. These water molecules are engaged into the system of H-bonding that helps molecules to pack into crystals.
- Four metal complexes – $\text{K}_2[\text{Cu}_3(\text{AACO})_4(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$, $\text{K}_2[\text{Cu}(\text{AACO})_2\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$, $[\text{Ni}(\text{AACO})(\text{H}_2\text{O})_3]_2 \cdot \text{H}_2\text{O}$ and $\text{K}_2[\text{Ni}_3(\text{AACO})_4(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ – were found to form a multimetallic dimeric and trimeric species. In all these cases the the AACO^{2-} dianions perform bridging function via the oxygen atoms of nitroso-group with the nitrogen atoms being part of the five-membered chelate rings. Three out of four complexes are anionic with, while one is neutral ($[\text{Ni}(\text{AACO})(\text{H}_2\text{O})_3]_2 \cdot \text{H}_2\text{O}$). Two trimetallic complexes are isostructural, with the *cis*-orientation of the AACO^{2-} dianions. Two bimetallic compounds $\text{K}_2[\text{Cu}(\text{AACO})_2\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$, $[\text{Ni}(\text{AACO})(\text{H}_2\text{O})_3]_2 \cdot \text{H}_2\text{O}$ are very different: the first one has *cis*-geometry of the cyanoximes in the anionic complex, while the second one just forms neutral dimeric complex with bridging dianion.
- Transition metals in polynuclear complexes have two different environments: penta- and hexa-coordinated, which corresponds to distorted square pyramidal and octahedral geometries.
- In all these Cu(II) and Ni(II) complexes there are both coordinated and crystallization water molecules. All are essential for the crystal packing via complex system of H-bonding.
- Careful heating of several Ni(II) complexes, such as $[\text{Ni}(\text{ACO})_2(\text{H}_2\text{O})_2]$, $[\text{Ni}(\text{2PCO})_2(\text{H}_2\text{O})_2]$, $[\text{Ni}(\text{PyrCO})_2(\text{H}_2\text{O})_2]$ and $[\text{Ni}(\text{PiPCO})_2(\text{H}_2\text{O})_2]$, at pre-determined by the DSC/TG analysis temperatures, allowed removal of coordinated water. The process is reversible for the first three complexes. Data of the XRD powder diffraction shows that in some cases the lattice is changed upon dehydration.

- Data of solid state electronic spectroscopy evidenced the retention of the geometry of central atoms during dehydration process in as [Ni(ACO)₂], [Ni(2PCO)₂], [Ni(PyrCO)₂] and [Ni(PiPCO)₂], which suggests developing bridging function of cyanoximes in the lattice upon water loss.
- Results of room temperature measurements of magnetic moment for the trimeric complex K₂[Cu₃(AACO)₄(H₂O)₄].4H₂O clearly indicates an extensive antiferromagnetic interactions between the cyanoxime-bridged metal centers.
- No one-dimensional solids were obtained at this point and all characterized by the X-ray analysis compounds possess columnar structures or represent 3D complex H-bonded networks. However, dehydration reaction clearly showed that the formation of stacks of complexes is feasible and arrangement of those in 1D solids achievable.

FUTURE WORK and project continuation:

Because of the time constrains we were unable to perform crystallization of the obtained anhydrous Ni(II) complexes [Ni(ACO)₂], [Ni(2PCO)₂], [Ni(PyrCO)₂] and [Ni(PiPCO)₂] in the presence of an inert organic solvent using an autoclave, or sealed ampoule method. When crystal structures will be determined then the binding mode of the cyanoximes in these complexes will be established, and it can be used for further design of conditions for the formation of 1D solids that form stacks. At that point the oxidation reactions to form mixed valence Ni(II)---Ni(III) coordination polymers will be conducted. As oxidants we plan to use H₂O₂ and organic t-butyl-hydroperoxide. The monitoring of the progress and studies of properties of such complexes will be done using the UV-visible and NIR spectroscopies. Hence, this work will be carried out in the group in the future.

Major peer-reviewed publications with Abraham Opalade:

Adedamola A. Opalade; Karmakar, A.; Rúbio, G.M.D.M.; Pombeiro, A.J.L.; Gerasimchuk, N. “Zinc Complexes with Cyanoxime: Structural, Spectroscopic, and Catalysis Studies in the Pivaloylcyanoxime–Zn System”. *Inorganic Chemistry*. **2017**, *56* (22), p.13962–13974.

Submitted for publication and passed peer-review process:

Adedamola A. Opalade, Carlos J. Gomez-Garcia, Nikolay Gerasimchuk. “New Route to Polynuclear Ni(II) and Cu(II) Complexes with Bridging Oxime Groups which are Inaccessible by Conventional Preparations”. *Crystal Growth & Design*, **2018**, December.

Manuscript in preparation:

Adedamola A. Opalade; Carlos Gomez-Garcia; O. Gerasimchuk; N. Gerasimchuk.
“Nickel(II) Aqua Complexes with Chelating Ligands: What Happens When Water is Gone?” will be submitted to the ACS journal *Inorganic Chemistry*, **2019**.

Presentations with Abraham Opalade:

50th Midwest Regional ACS Meeting (October 21-24, 2015; St. Joseph, MO)

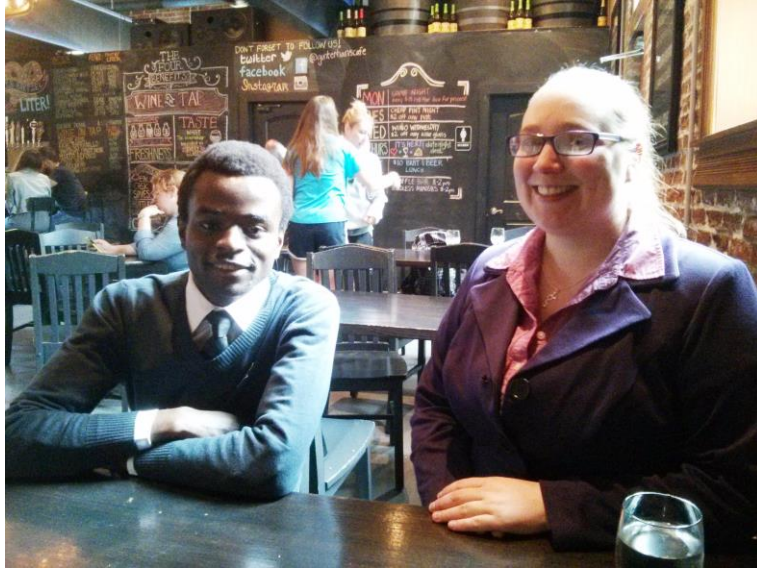
Opalade, A.A.; Gerasimchuk, N. “Investigating crystallohydrates of Ni and Zn cyanoximes coordination compounds.” Oral presentation, #115.

Now, some photos from our travel to conferences, presentations, holidays...

21st Missouri Inorganic Day : UM-Columbia, May 2015



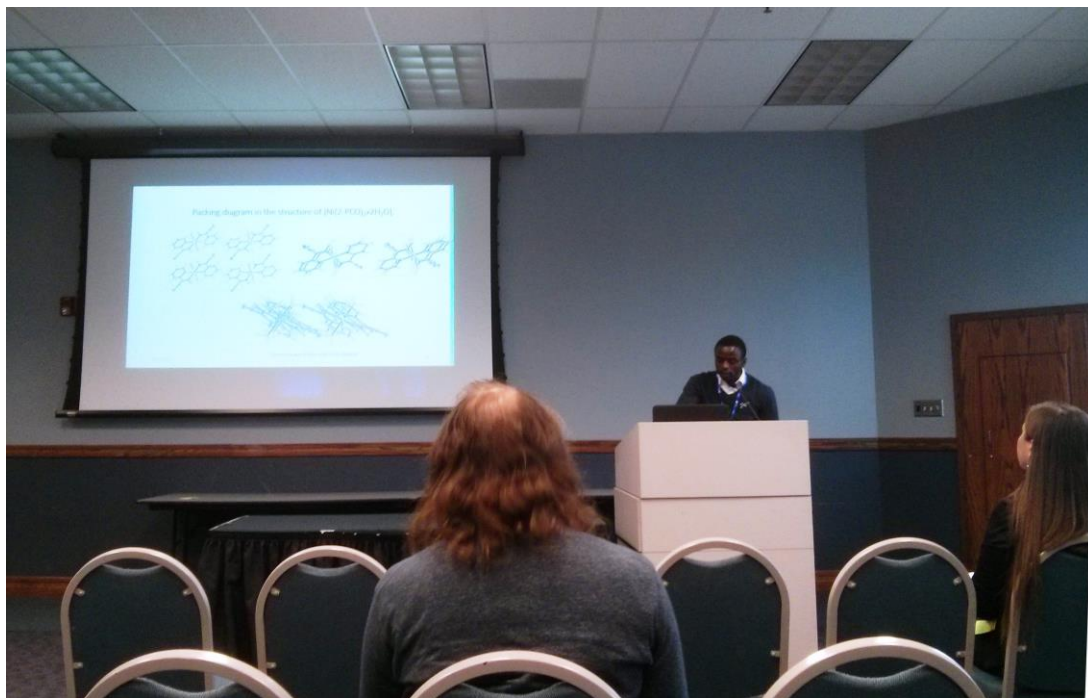




Trip to the state capital – Jefferson City, Capitol Building.



Participation and presentation at the Regional ACS Meeting in St. Joseph, MO: October 2015.





Mid-south Inorganic Chemists Association (MICA) meeting in April of 2016 at Missouri State University.





Graduation!



Honorable lunch with parents (May 2016)