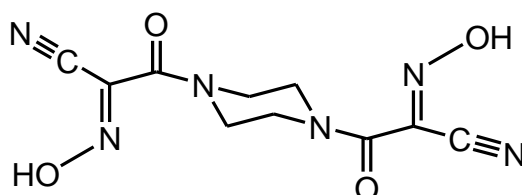




Carl Cheadle: MS 2008

Thesis "Synthesis and Studies of N¹,N²-Piperazine-bis-(2-oximino-2-cyano)acetamide and its Several Metal Complexes."

Carl spent in my research laboratory three years and generated enormous amount of data both in synthetic part of his project, and in characterization of a series of new compounds using spectroscopic and structural methods. His project was a continuation of preparative work initiated by Daniel Eddings (MS degree, 2003) and Jessica Ratcliff (MS degree, 2007). Carl Cheadle's project was dedicated to the preparation of a *new chelating bis-cyanoxime* – derivative of piperazine abbreviated by us as H₂BiPipCO – chemical structure of which is shown below.



In context of previous work with mono-cyanoximes and their Pt-compounds it was interesting to prepare aforementioned novel bis-cyanoxime and its Pt-complex. We expected to see a considerable difference in compound's structure and its properties. Resulting coordination polymer could be very interesting for potential applications in molecular electronics and for the pursuit of a one-dimensional high-temperature superconductor in particular. Thus, making new complex in which a partial oxidation of the metal centers can be introduced, makes "electron hopping" between Pt(II) and Pt(IV) centers in formed mixed valence very feasible in the "metal wire" (Figure 1). Bulky organic outward pointed groups generate protective casing for the conductive wire.

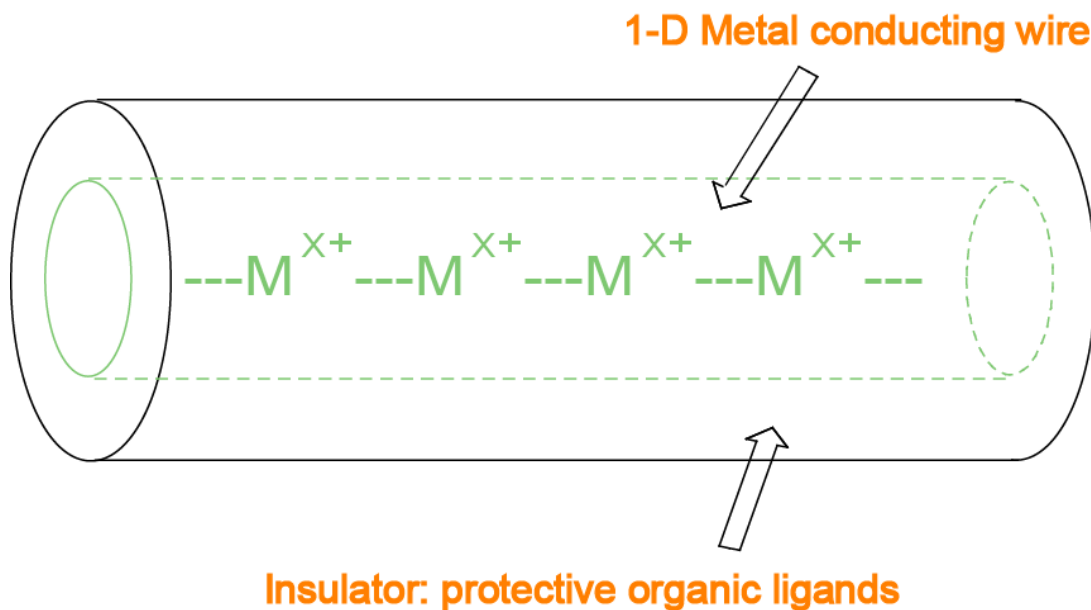


Figure 1. Schematic representation of the structure of 1D mixed valence Pt(II) coordination polymer with introduced Pt(IV) "impurity".

Similar Pt-based "poker chips" type stacks were obtained previously by other investigators using partially oxidized tetra-cyanoplatinates (POCP), or MX solids in which Pt(II) and Pt(IV) centers are preassembled at 1:1 ratio.

Specifically, we set out to synthesize a two-dimensional platinum cyanoximate polymer by using a symmetrical organic ligand capable of binding platinum metal ions at both termini, which design of the H₂BiPipCO provided.

MS thesis ABSTRACT

Acetamide – cyanoximes having the general formula NC-C(R)=NOH , where R is a substituted acetamide, have shown interesting biological activities such as growth regulation in plants and effectiveness as organophosphorous pesticide antidotes. Platinum(II) compounds of these cyanoximates earlier showed promising *in vitro* anti-cancer activity against human cancers as well as potential for material science applications.

It was found that platinum(II) cyanoximates form one-dimensional polymers with direct Pt---Pt bonding that allows for electronic communication and conductivity between metal centers. These compounds present interesting possibilities for further development into two-dimensional polymers and for adjustment of Pt---Pt bond length due to varying cyanoximate substituent sizes. Obtained Pt(II) complexes were chemically oxidized in solutions (with Br_2 and AgPF_6) and mixed valence Pt(II)---Pt(IV) species were formed. A new bridging bidentate ligand, $\text{H}_2\text{BiPipCO}$, was synthesized and characterized, as well as its nickel triad complexes. Additional experiments involved the syntheses and characterizations of a bulky ligand N,N-dicyclohexyl acetamide cyanoxime and its platinum complex.

KEYWORDS: platinum, cyanoximes, one-dimensional coordination polymers, square-planar, metallophilic interactions.

The synthesis of H₂BiPipCO represents simple two steps procedure displayed in Figure 2. Since obtained in the first step substituted bis-acetonitrile is not reactive towards the nitrosation reaction at acidic conditions, Carl had to use gaseous methylnitrite CH₃-ONO at basic conditions in order to assure generation of the bis-cyanoxime. Some important actual details of the synthesis are presented in Figure 4. Synthesized ligand according to the NMR data exists as a mixture of diastereomers as shown in Figure 3.

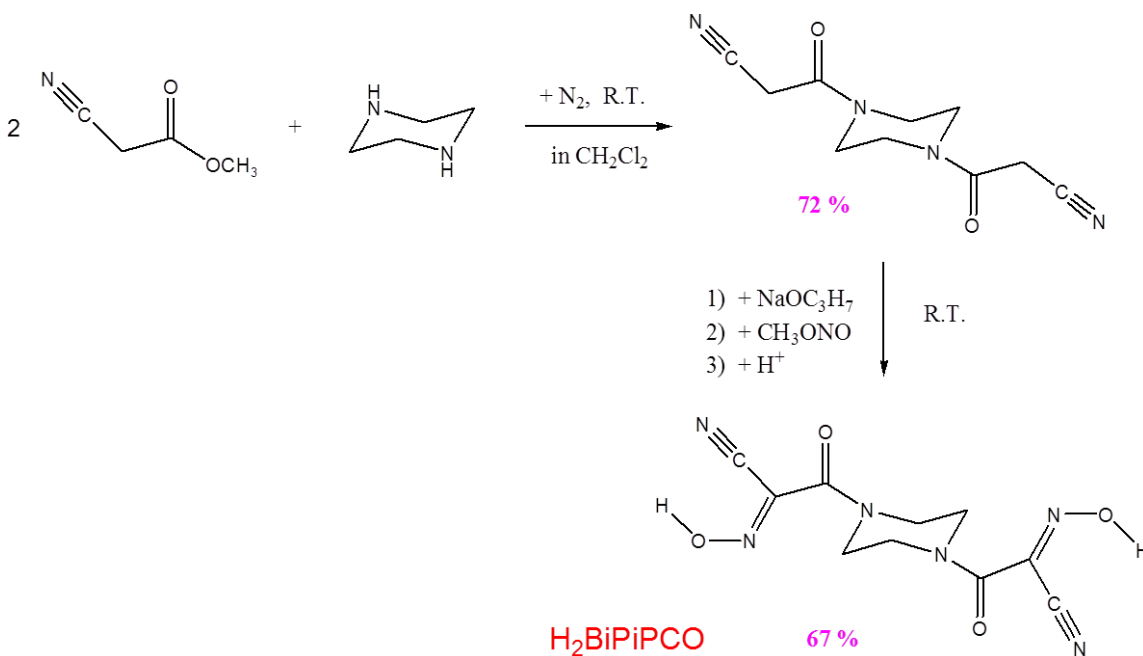


Figure 2. Schematic depiction of preparation of new bis-cyanoxime.

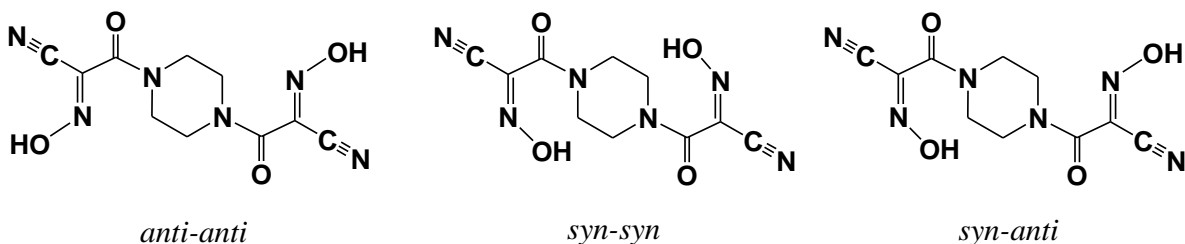


Figure 3. Geometrical isomerism in H₂BiPipCO that was established by ¹H and ¹³C{¹H} NMR spectroscopy.

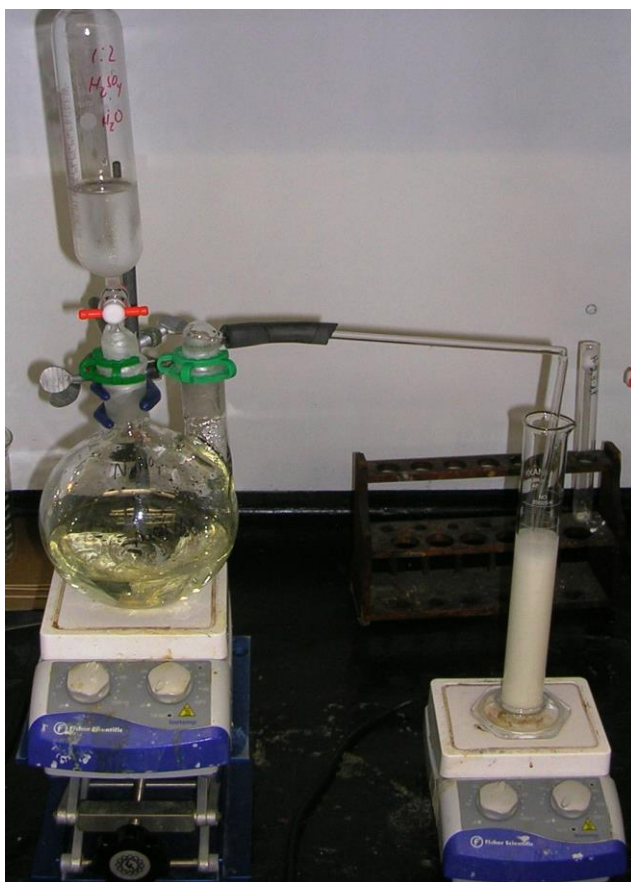
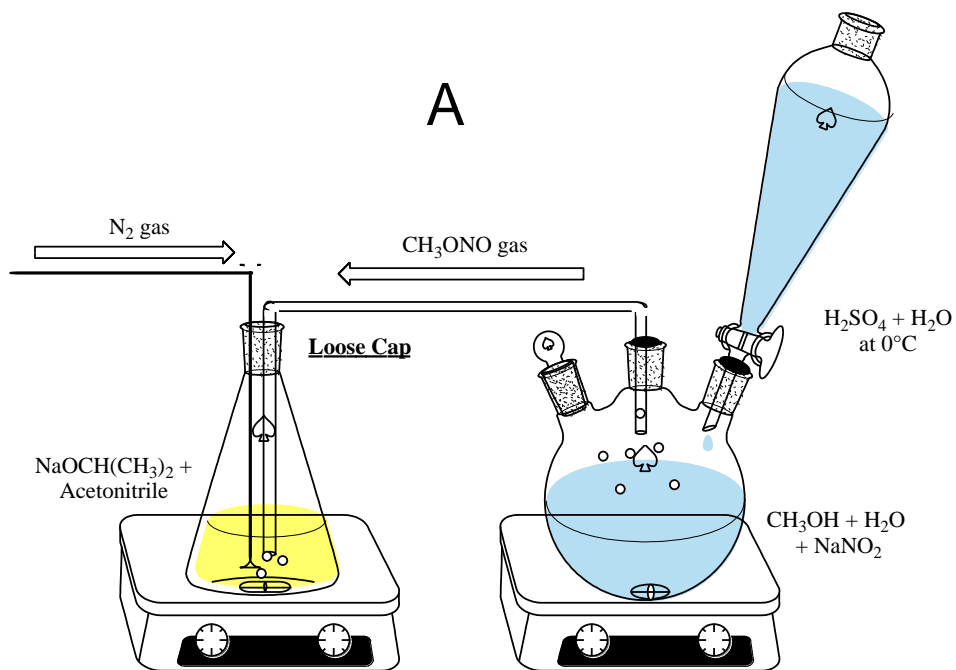


Figure 4. Experimental scheme (A) and actual experimental setup used (B) for the generation of methyl nitrite for the oximation of deprotonated acetonitriles under basic conditions.

It took almost three years to crystallize the ligand and obtain suitable for the X-ray analysis single crystals! It turned out that in the $H_2BiPipCO$ crystallized as a mixture of two syn/anti diastereomers at 50:50 ratio on both ends of the molecule as shown in Figure 5A. Crystal packing was found to be rather interesting because of a very similar geometry for the H-bonding for both isomers that tolerates small changes in angles in the C-N-O fragments (Figure 5B).

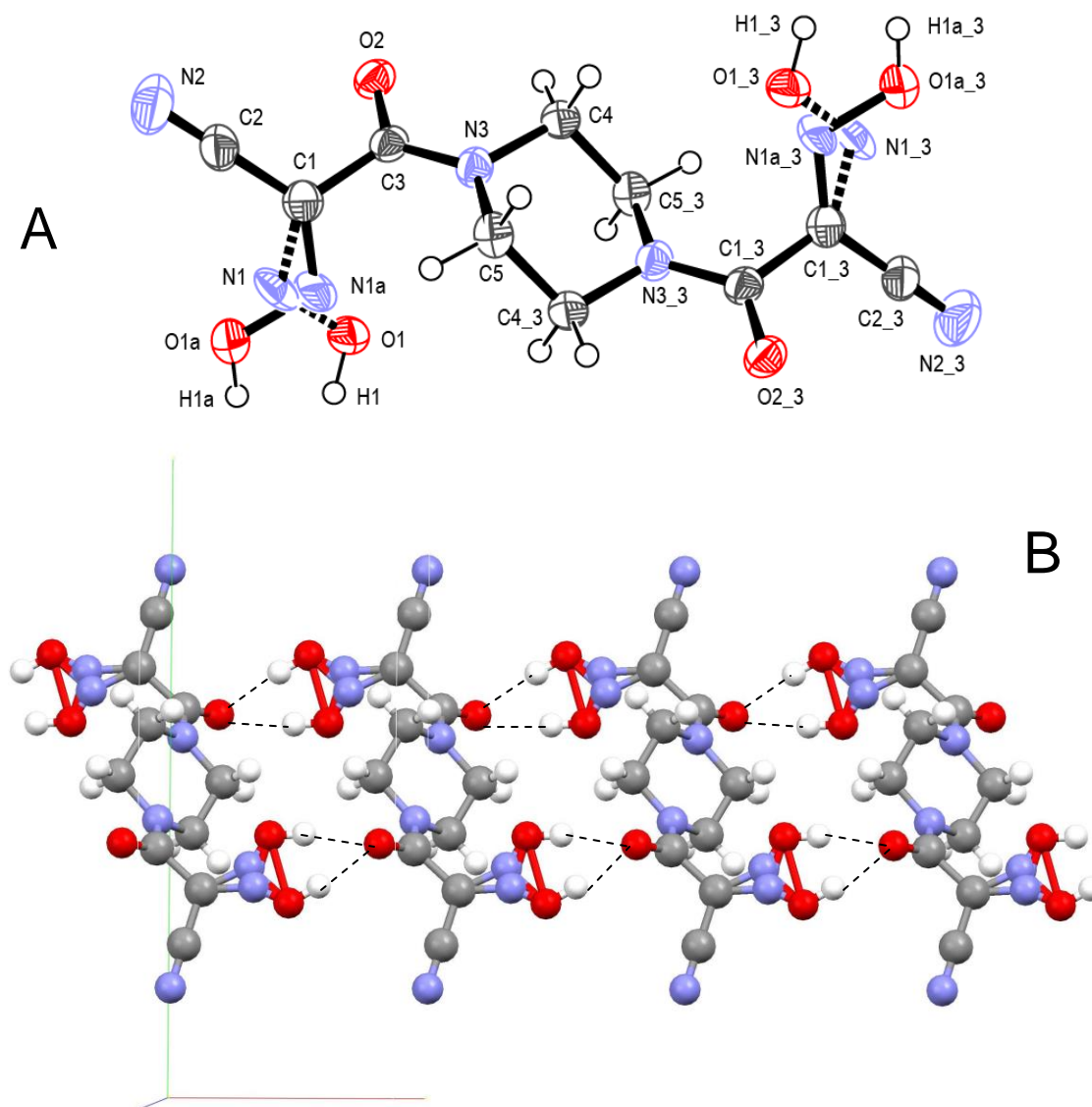


Figure 5. Molecular structure and numbering scheme for the crystal structure of $H_2BiPipCO$ (A), and prospective view of the column of compound along c direction (B).

Newly synthesized bis-cyanoxime was studied in aqueous solution and its pKa values were measured. As expected, the new cyanoxime ligand H₂BiPipCO undergoes independent stepwise deprotonation in solutions as a weak acid:



Values of pKa1 and pKa2 were found to be 4.76 ± 0.02 and 5.61 ± 0.02 respectively, which are in line with those for previously determined cyanoximes.

Carl also investigated the reaction between secondary amines and cyanoacetic acid esters (methyl and ethyl) as displayed in Figure 6. To our greatest surprise, depending on conditions of reactions three different outcomes were obtained. All three products **1** – **3** were observed and their structures confirmed using the X-ray analysis. As Carl clearly showed only product **3** is desired substituted acetonitrile with amide functionality, which was possible to further transform into desired cyanoximes **4**.

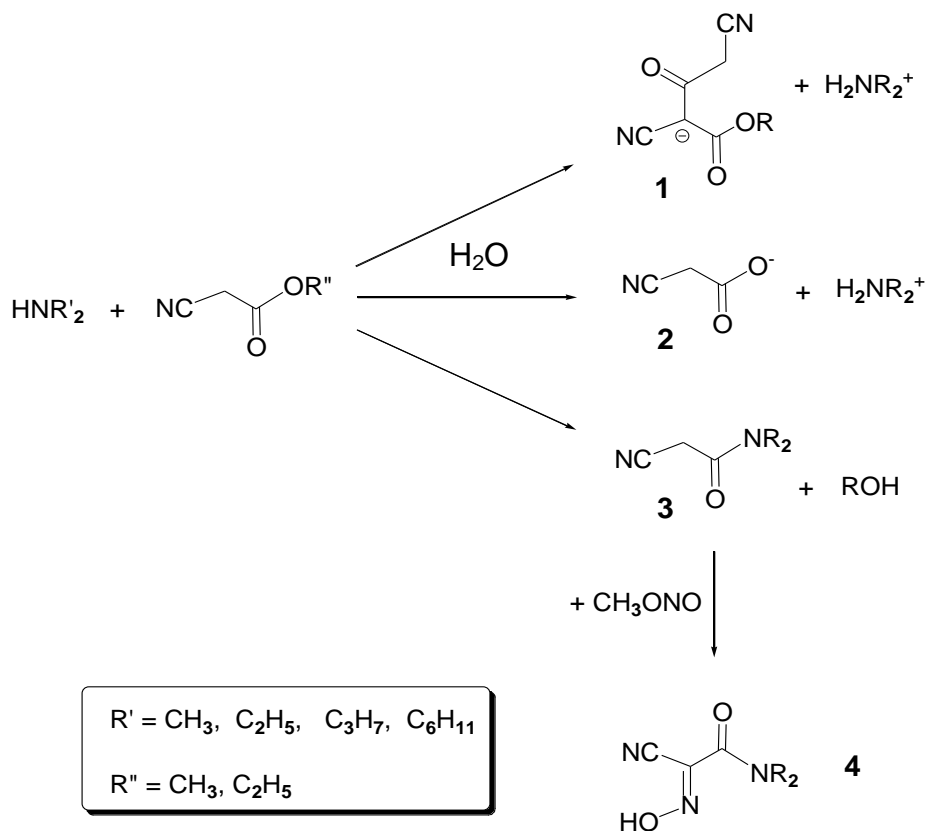
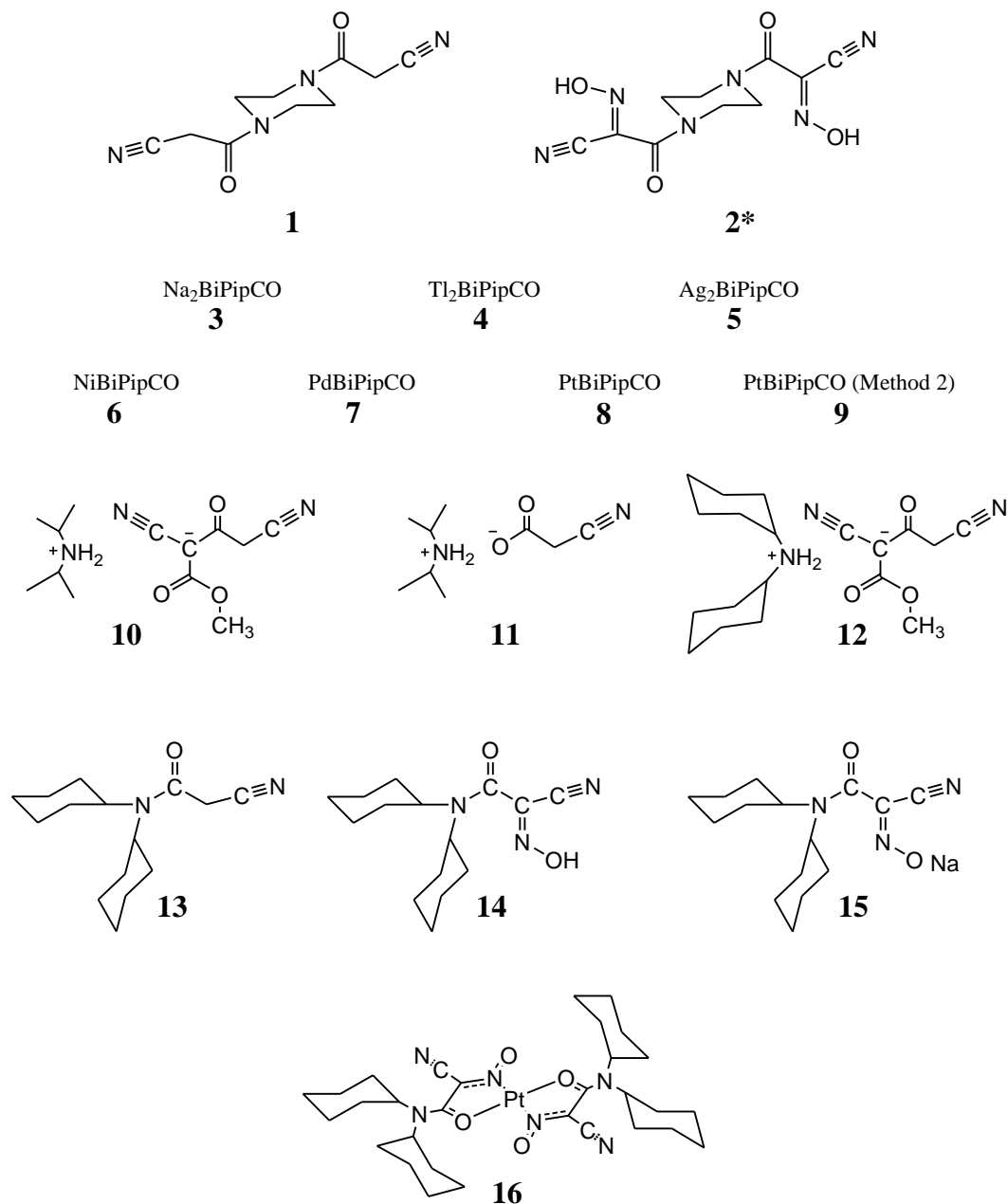


Figure 6. Reaction schemes for bulky amines with cyano-esters, with all possible products.

Using those cyanoximes **4** Carl Chedale was able to prepare a series of compounds listed in Figure 7 along with their used abbreviations. All synthesized compounds underwent subsequent characterization using elemental analysis (by combustion method on C,N,H content), a variety of spectroscopic methods and, pending on availability of suitable single crystals, the X-ray analysis.



*The deprotonated form of this species is referred to as BiPipCO^{2-} anion

Figure 7. Chemical species synthesized and studied during this research project. Compounds' numbers are shown in Times New Roman type font in bold.

The deprotonation of H₂BiPipCO by bases in water gives light-yellow solution of the dianion as shown in Figure 8 with a weak band ($\epsilon = 60$) at ~400 nm for the $n \rightarrow \pi^*$ transition.

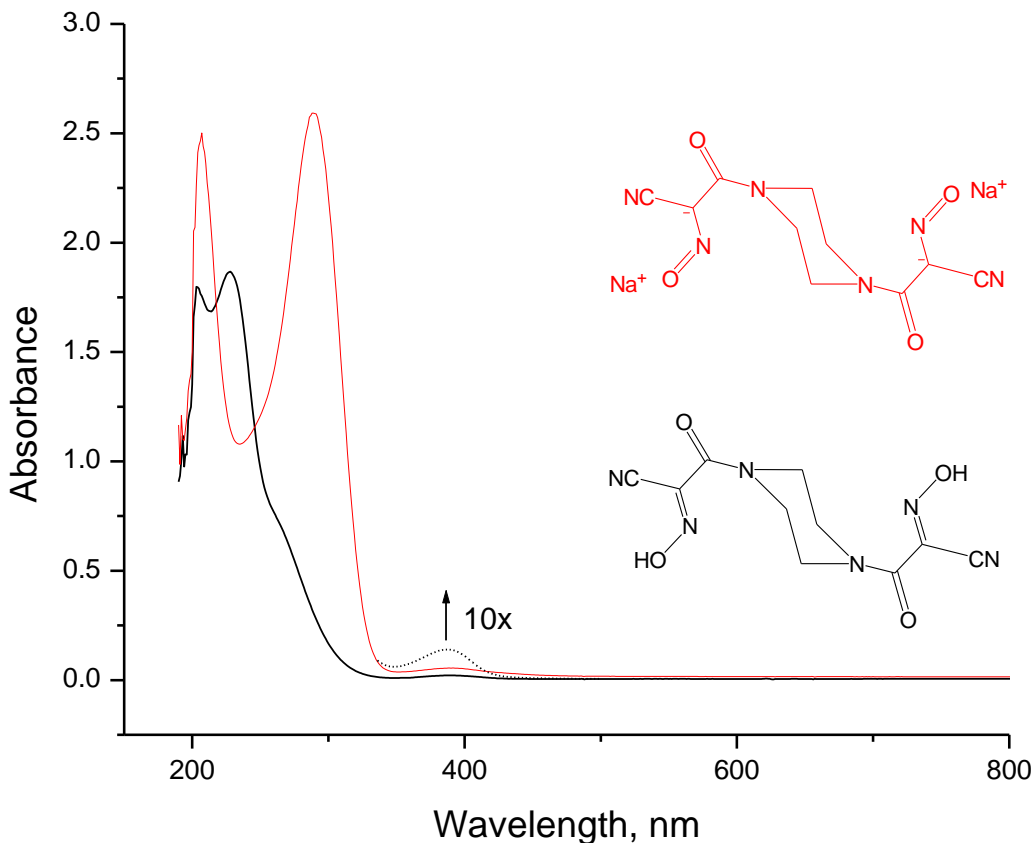


Figure 8. Spectra of protonated (2) and deprotonated (3) forms of H₂BiPipCO in the UV-visible spectra in ethanol. Quartz cuvette path length: 1 cm.

Alkali metal, Tl⁺ and Ag⁺ salts of the BiPipCO²⁻ dianion were obtained by Carl, but the first group proved to be very hygroscopic. Nevertheless, in aqueous solutions pronounced solvatochromic behavior of the dianion was observed (Figure 9) and was found to be similar to that for other known and studied cyanoximes. The general trend was confirm for this cyanoxime as well: polar aprotic solvents induce pink color in the dianion with a band around 470 nm, while ROH solvents capable of the H-bonding with the oxime fragments generate yellow solutions with bands positioned less than 400 nm (Figure 9).

The IR spectra for all compounds that Carl made are summarized in Table 1. There are also present tentative assignments of vibrational bands observed in spectra.

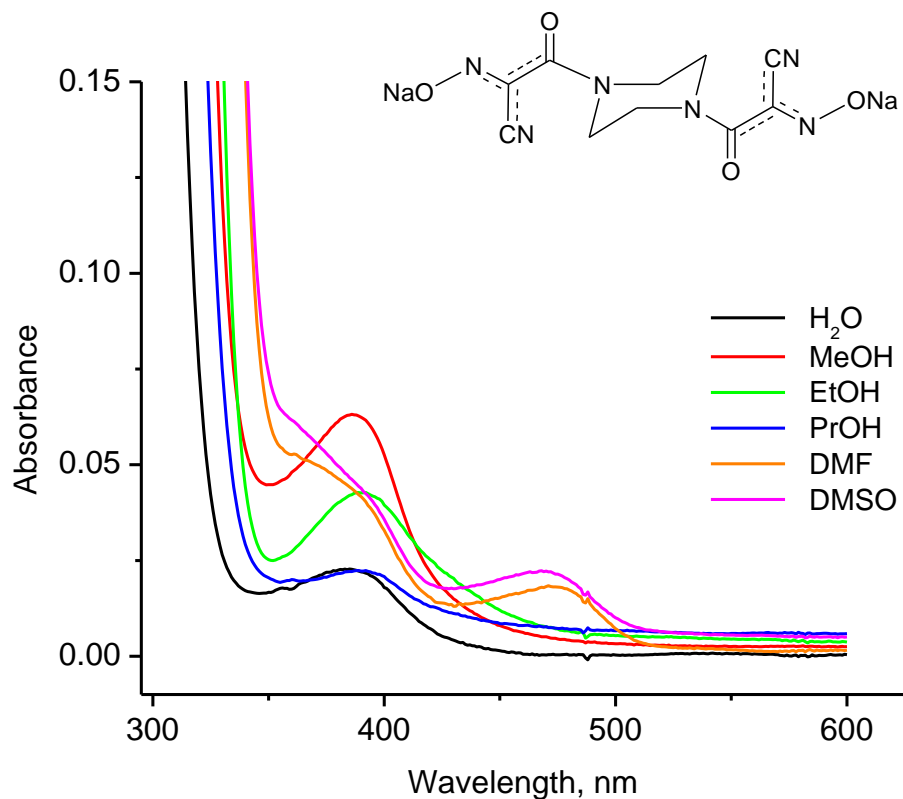


Figure 9. Solvatochromatic series for $\text{Na}_2\text{BiPipCO}$ (compound **3** in Figure 7) in different solvents; $T=296\text{ K}$, 1 cm glass cuvette.

Table 1. IR-spectroscopic data for solid samples of BiPipCO^- -containing compounds.

Compound	Assignment of frequencies, cm^{-1}					
	$\nu^{\text{as}}\text{CH}$	$\nu^{\text{s}}\text{CH}$	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{O})$	$\nu^{\text{s}}\text{NO}$	$\nu^{\text{as}}\text{NO}$
2 , $\text{H}_2\text{BiPipCO}$	3175 3124	2971 2813	2232 2243	1625	1047	1176
3 , $\text{Na}_2\text{BiPipCO} \cdot 4\text{H}_2\text{O}$	2925	2859	2218	1617	1136	1276
4 , $\text{Tl}_2\text{BiPipCO}$	*	*	2207	1576	1170	1310
5 , $\text{Ag}_2\text{BiPipCO} \cdot 2\text{H}_2\text{O}$	*	*	2206 2228	1585	1215	1340
6 , $\text{NiBiPipCO} \cdot 4\text{H}_2\text{O}$	2926	2865	2218	1586	1172	1291
7 , $\text{PdBiPipCO} \cdot 4\text{H}_2\text{O}$	2925	2860	2213	1558	1154	1291
8 , $\text{PtBiPipCO} \cdot 5\text{H}_2\text{O}$	2920	2865	2213	1569	1159	1286

* C-H bands in silver and thallium compounds are obscured by the mulling agent.

Based on conducted investigation Carl proposed the following structures for the Ni-triade metals as shown in Figure 10. However, without direct support from crystallographic studies offered geometries are only suggestive. No photoluminescence studies from Pt-based complexes **8** and **9** (Figure 7) were carried out yet.

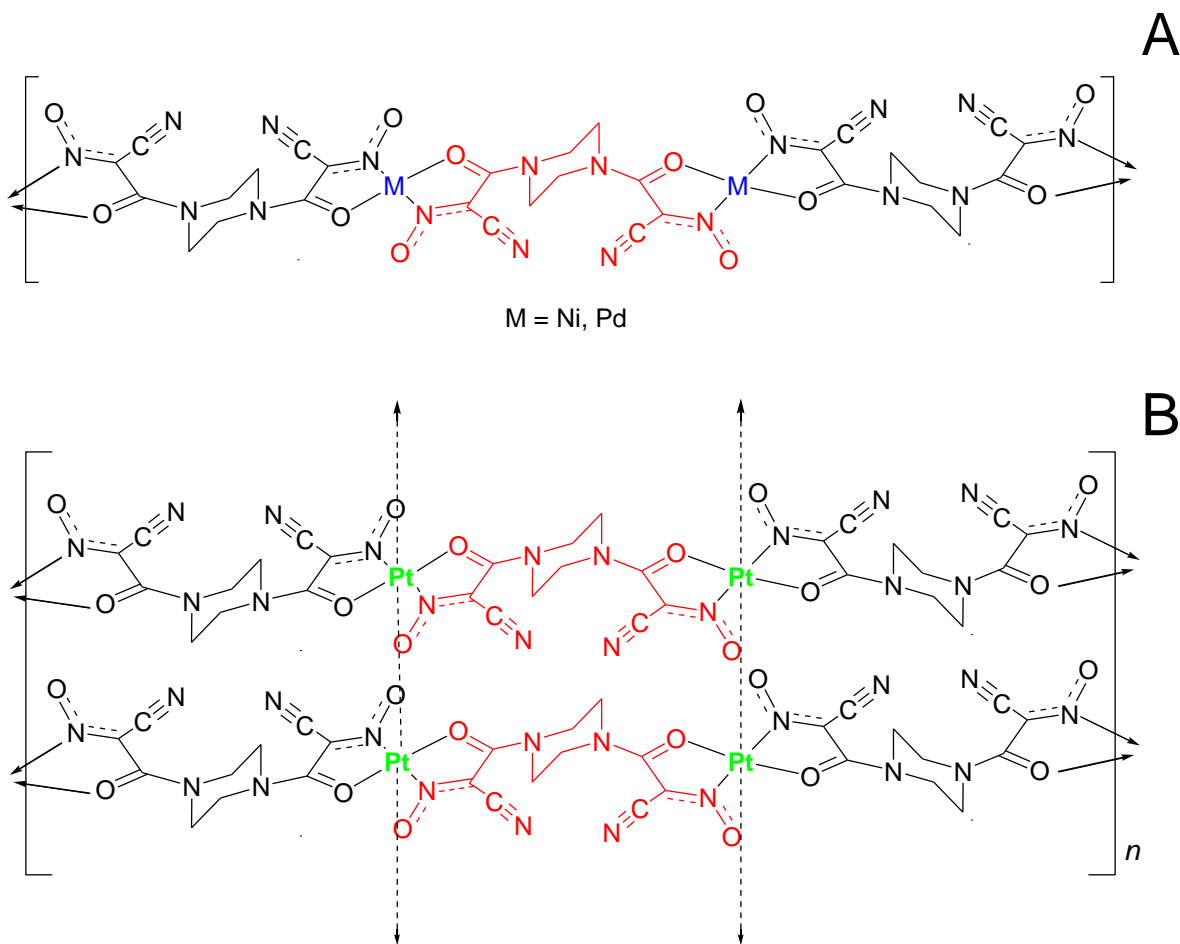


Figure 10. Suggested structural formulas for bivalent 1D and 2D polymers of Ni/Pd (A) and Pt (B), respectively. One cyanoxime ligand is shown in red to highlight the bridging effect of BiPipCO²⁻ dianion in building the polymeric structure.

CONCLUSIONS from Carl Cheadle's work:

1. The synthesis of bivalent nickel triad cyanoximate complexes was completed. These compounds were characterized by the CHN, AAS, and ICP-AES elemental analyses, and the infrared spectroscopy.
2. The synthesis of a bulky acetamide cyanoximes was completed and characterized by the UV-Visible, NMR and IR-spectroscopy as well as the X-Ray diffraction studies.
3. The reaction of a bulky secondary amine with a cyano-ester produces a conjugated carbanion, rather than an amide.
4. The synthesis of a two-dimensional platinum(II) cyanoximate polymer was completed. The 2D polymer network leads to greatly decreased solubility and, perhaps, higher-energy of the Pt---Pt bonds in the coordination polymer held together by metallophilic interactions.
5. Platinum(II) acetamide cyanoximates with bulky ligands do not exhibit Pt---Pt bonding.
6. The fractional chemical oxidation of Pt(PiPCO)₂ leads to lower-energy Pt---Pt bonds.

Major peer-reviewed publications with Carl:

Cheadle, C.; Ratcliff, J.; Berezin, M.; Pal'shin, V.; Nemykin, V.N.; Gerasimchuk, N. "Shortwave infrared luminescent Pt-nanowires: a mechanistic study of emission in solution and in the solid state". *Dalton Transactions*, **2017**, 46(39), 13562-13581.

Cheadle, C.; Gerasimchuk, N.; Barnes, C.L.; Tyukhtenko, S.I.; Silchenko, S. "First bis-cyanoxime: synthesis and properties of a new versatile and accessible polydentate bifunctional building block for coordination and supramolecular chemistry" *Dalton Transactions*. **2013**, 42 (14), p. 4931 – 4946.

Presentations with Carl:

42nd Midwest Regional ACS Meeting (November 7-10, 2007; Kansas City, MO)

Cheadle, C.*; Gerasimchuk, N.; Kolesnichenko, V.; Ratcliff, J. "Nickel triad complexes of the amide-cyanoximes containing N-morpholy-, N-piperidine- and bis-N-piperazine groups."

Proceedings of 42nd Midwest Regional Meeting of the ACS, p.138.

Marcano, D.*; Nemykin, V.; Barnes, C.; Domasevitch, K.V.; Gerasimchuk, N. "Pyridylcyanoximes and their metal complexes".

Proceedings of 42nd Midwest Regional Meeting of the ACS, p.139.

43rd Midwest Regional ACS Meeting (October 8-11, 2008; Kearney, NE)

Cheadle, C.*; Keene, M.; Gerasimchuk, N. "Synthesis and characterization of several cyanacetamide-oximes and their Pt(II) and Pd(II) complexes." Proceedings of 43rd Midwest Regional Meeting of the ACS, talk #45, p.63.

45rd Midwest Regional ACS Meeting (October 27-30, 2010; Wichita, KS)

Ratcliff, J.* Kolesnichenko, V.; Berezin, M.; Pal'shin, V.; Cheadle, C.*; Gerasimchuk, N. "Pt cyanoximates: self-assembled nano-size electrical conductors." Proceedings of 45rd Midwest Regional Meeting of the ACS, poster #383, p.42 of the program booklet.



Graduation!

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

21st Missouri Inorganic Day : UMKC, 2007



Visit of the Nelson-Atkins Art Gallery in Kansas City.



...thinkers...



Midwest Inorganic Chemists Association meeting, Fall 2007



Midwest Regional ACS meeting, Fall 2008

