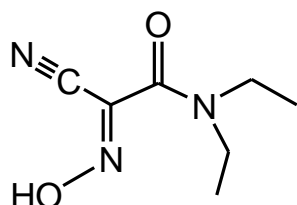




Danielle Klaus, 2012-2014

Danielle Klaus came to my research group by her desire to start working on some meaningful project after she took my CHM 375 Inorganic Chemistry class. She also enrolled at first in my research courses CHM 399 and CHM 499 and worked in my research laboratory for almost three years. Danielle received the project to develop coordination chemistry of newly made cyanoxime ligand H(DECO) [by Matthew Keene], who left the group a couple of years before. This was exciting time of absolutely new studies and exploration of chemistry of bivalent Pd and Pt of that new cyanoxime ligand of the amide type:



H(DECO)

or 2-oximino-2-cyano-N,N'-diethyl-acetamide

Thus, Danielle used left from Matt several grams of the new ligand and studied its pK value and spectroscopic properties. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed signals for all 7 carbon atoms, which immediately indicated the absence of rotation in the amide group which leads to non-equivalence of the two ethyl- groups (Figure 1). The most interesting endeavor was recording of variable temperature ^1H NMR spectra and determination the rotation energy barrier as explained in Figure 2. Thus, pKa value for this new cyanoxime was determined (with the help of Dr. S. Silchenko) to be 5.622 ± 0.03 , which is in line with other amide-based cyanoximes of similar structures (Figure 3).

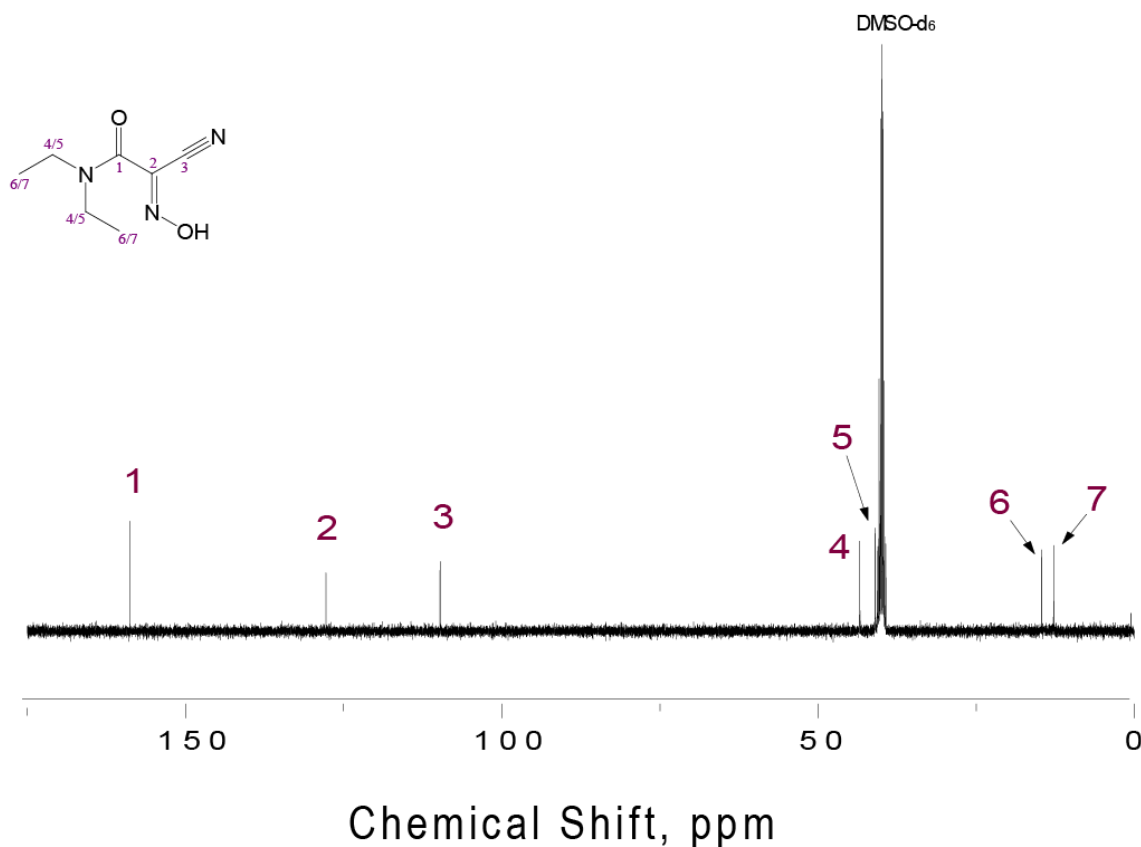


Figure 1. Room temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of H(DECO) in dmsO- d_6 showing two non-equivalent ethyl groups of the amide fragment.

Deprotonation of H(DECO) by bases in aqueous and non-aqueous solutions leads to the formation of yellow-colored DECO $^-$ anion in which the delocalization of the negative charge in the core can be described by several resonance forms as shown in Figure 4 below.

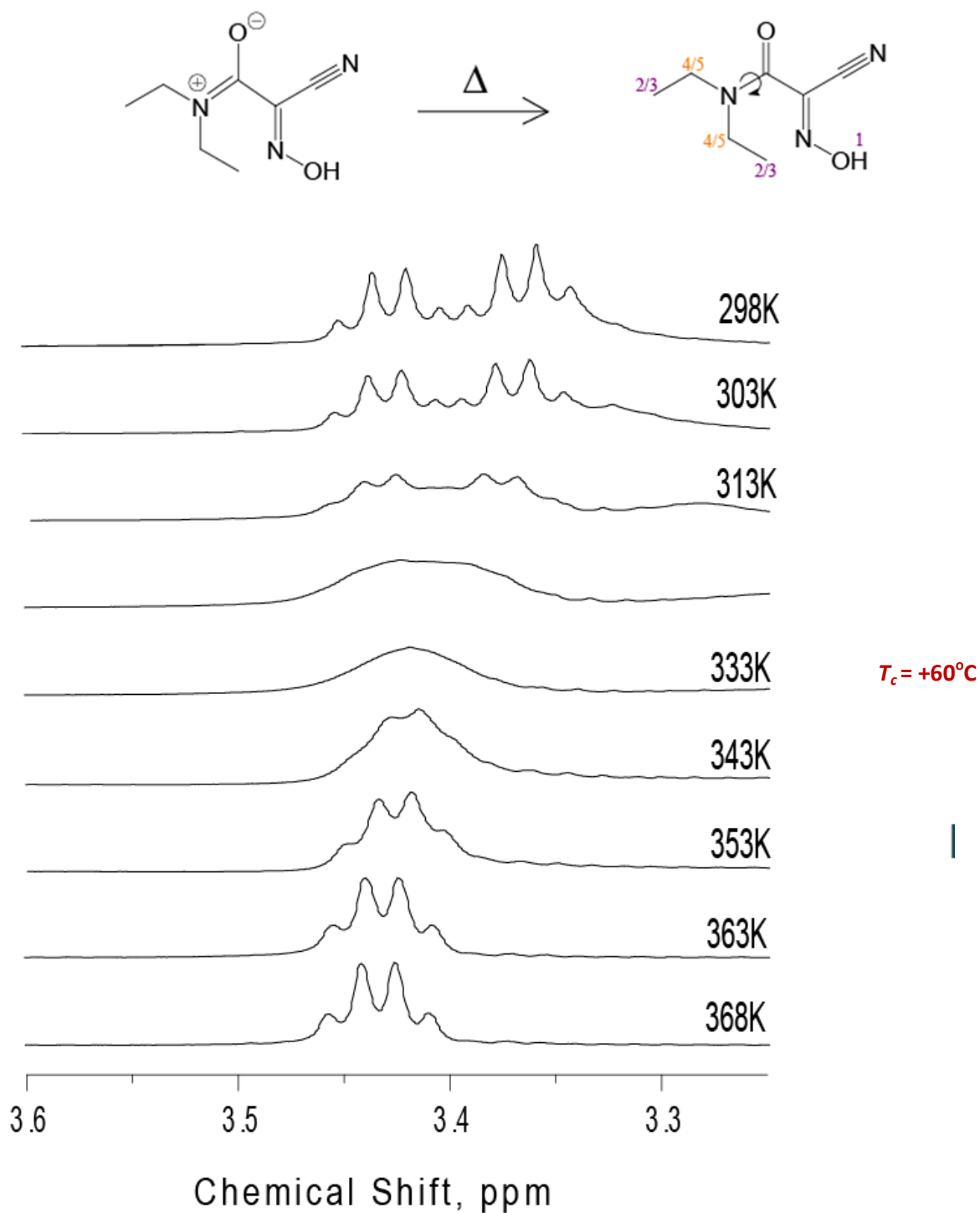


Figure 2. Variable temperature ^1H NMR experiments: fragment of the methylene group region in spectra of HDECO in dms0-d_6 solution.

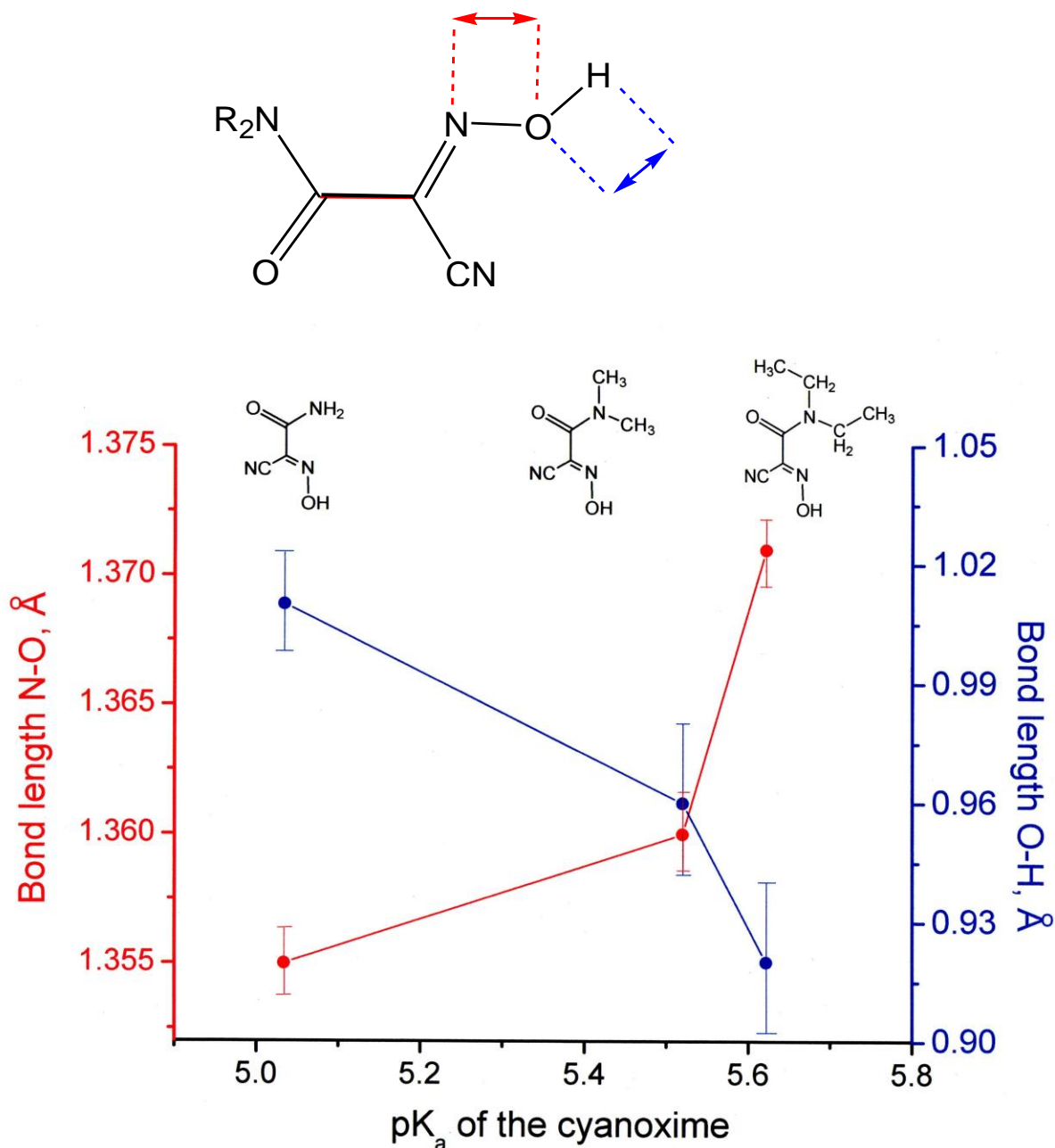


Figure 3. Correlations between bond lengths in the oxime fragment and pK_a values of the amide-based cyanoxime.

The anion of DECO⁻ is an excellent ligand and forms complexes with metals of Ni-triade series. Danielle prepared both Pd and Pt complexes of this new cyanoxime that have M(DECO)₂ composition using route shown in Figure 5 below. Actual microscope photographs of bulk

samples of these compounds appearance are shown in Figure 6. It turned out that the Pt(DECO)₂ complex exists as three differently colored polymorphs (Figure 7)!

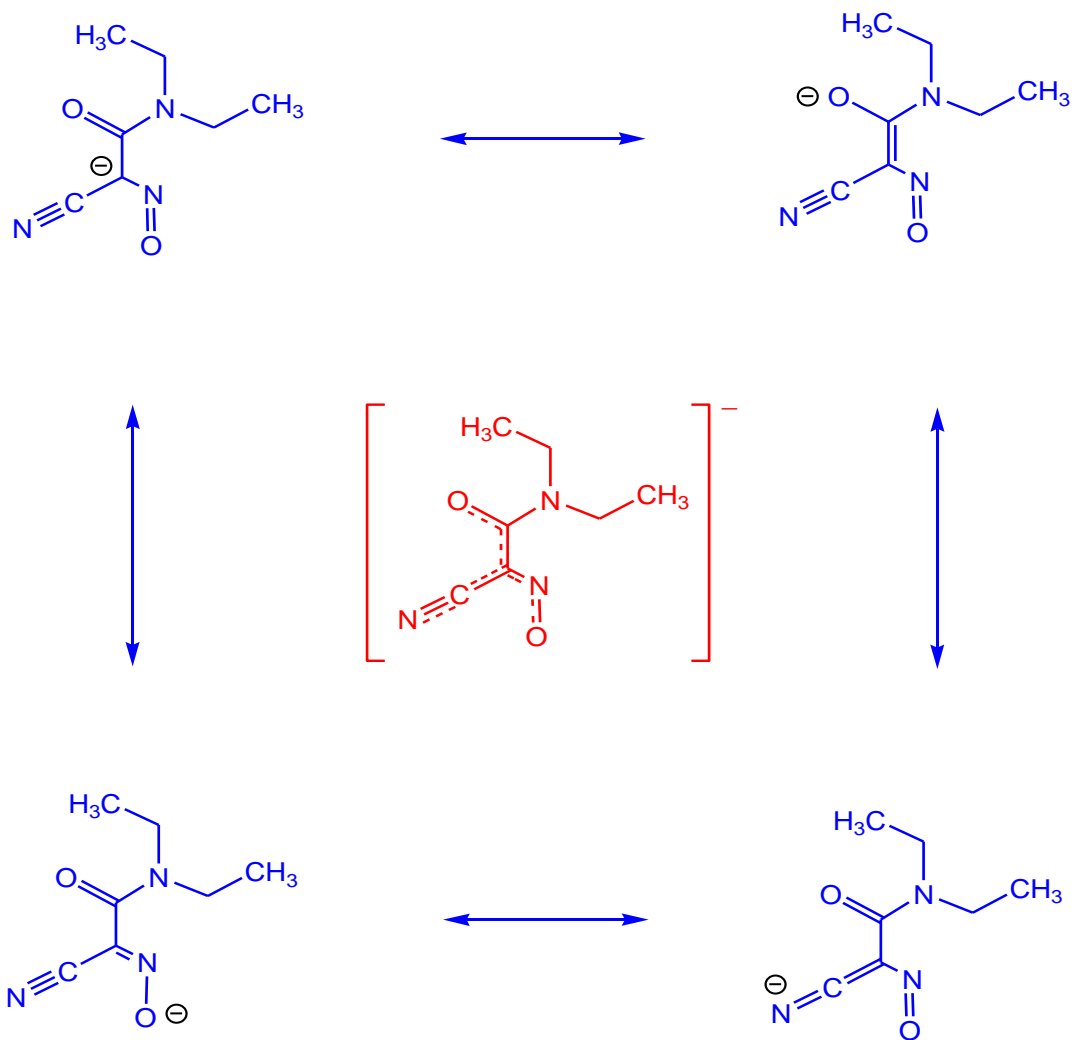


Figure 4. Delocalization of negative charge throughout DECO⁻ anion showing that three out of four resonance forms have nitroso- character.

Microscope photographs of single crystals of all three polymorphs are presented in Figure 8. Danielle carefully grew up single crystals of Pd(DECO)₂, and two polymorphs of Pt-DECO system: yellow monomeric and red dimeric [Pt(DECO)₂]₂ (Figures 6 and 7). Thus, crystal structures were determined and presented in Figure 10-12.

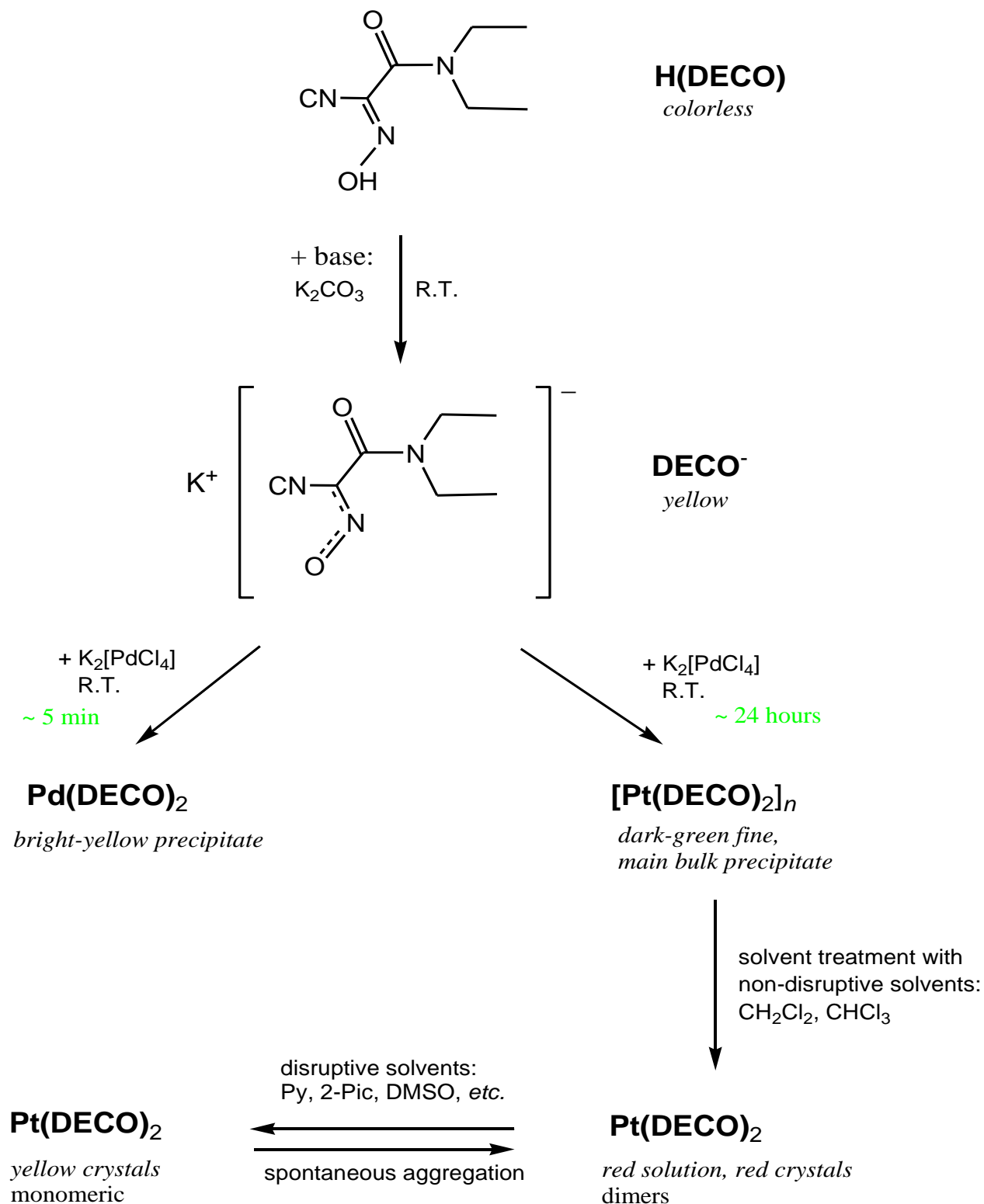


Figure 5. Synthetic route to Pd,Pt-derivatives of the H(DECO).

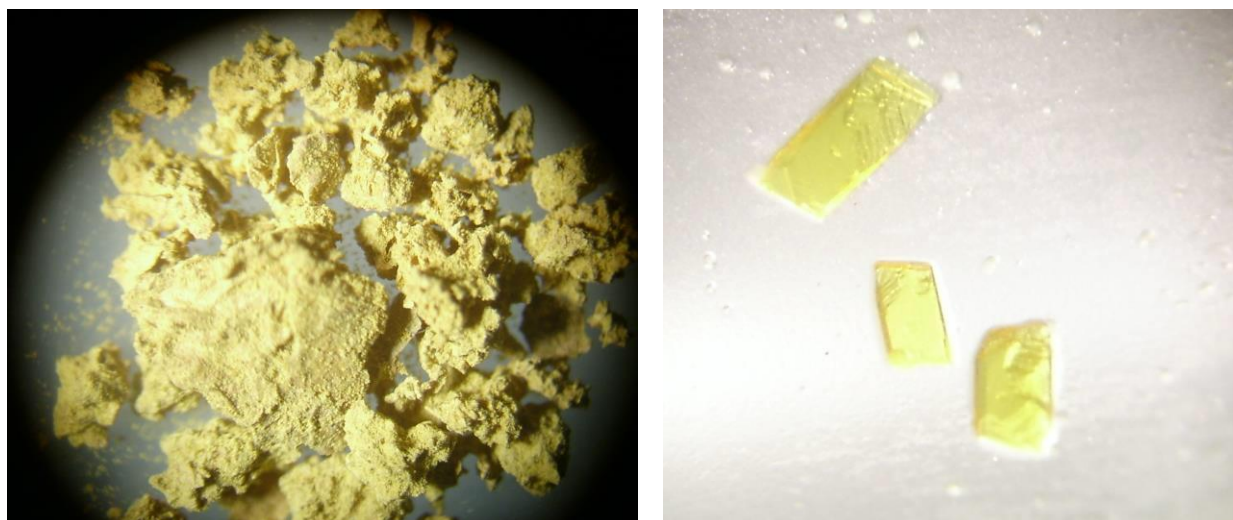
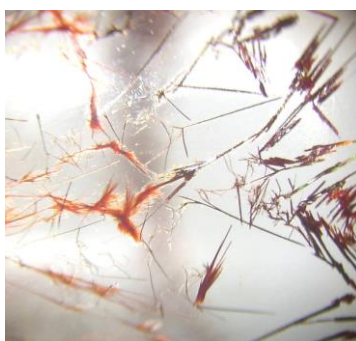


Figure 6. Actual photographs of Pd(DECO)₂ powder sample and single crystals.



green 1D coordination polymer



red and



yellow monomeric form used for the X-ray analysis.

Figure 7. Three different forms of the “Pt(DECO)₂”

Despite numerous attempts, suitable for the X-ray analysis diffracting single crystals of a dark-green polymorph were not isolated. The coordination polymeric nature of this complex was inferred from its dichroic nature very similar to that for classic 1D coordination polymers such as KCP and MX mixed valence compounds. That particular optical feature unmistakably suggested that Danielle’s green Pt(DECO)₂ complex is also a polymer in nature.

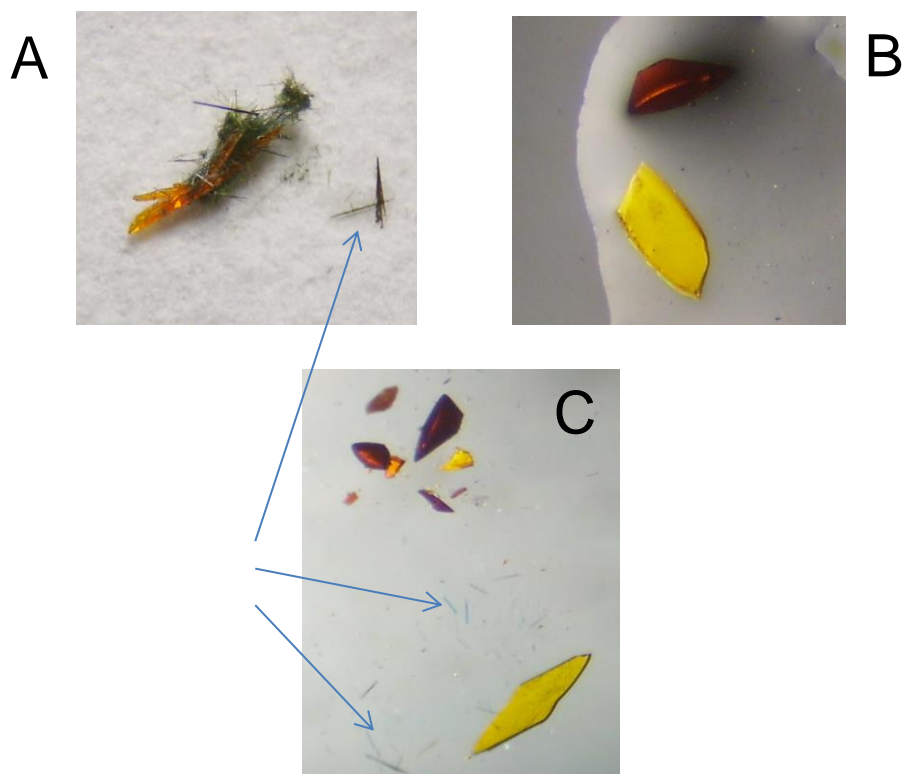


Figure 8. Actual microscope pictures of three polymorphs of $\text{Pt}(\text{DECO})_2$ complex: A – yellow monomer and needles of the green 1D-polymer, shown by arrows, B – yellow monomer and red dimer, C – all three polymorphs in one eye view.

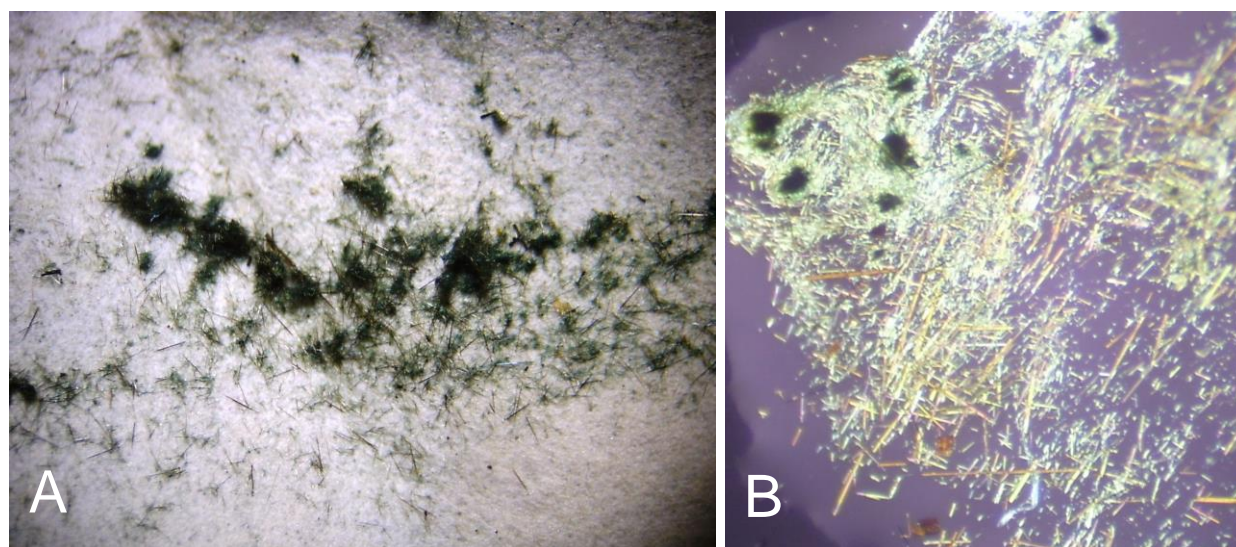


Figure 9. Actual microscope pictures of dark-green dichroic needles $[\text{Pt}(\text{DECO})_2]_n$ in reflected light (A) and transmitted light (B).

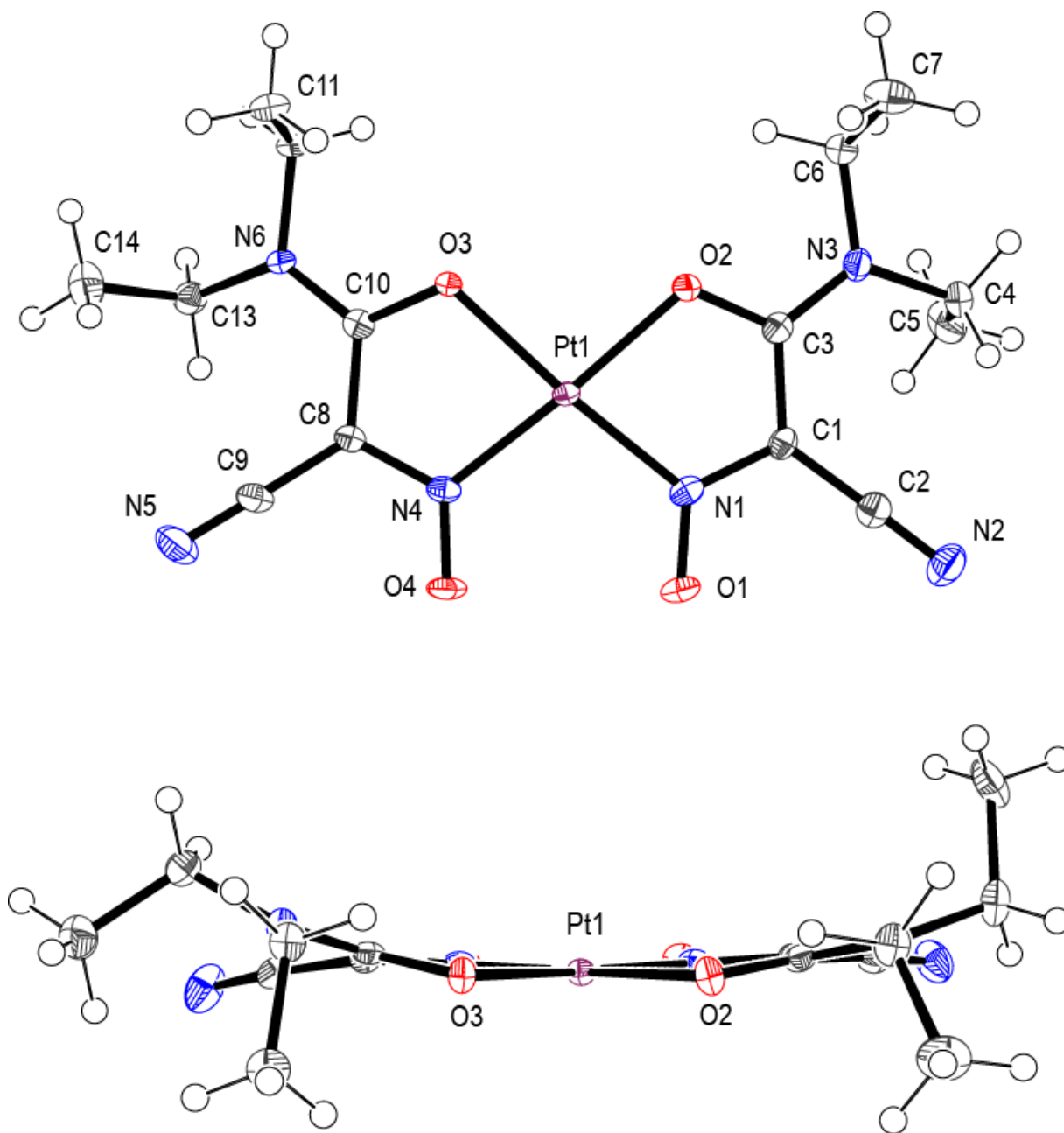


Figure 10. Top, side views and the numbering scheme in the structure of yellow, monomeric Pt(DECO)₂.

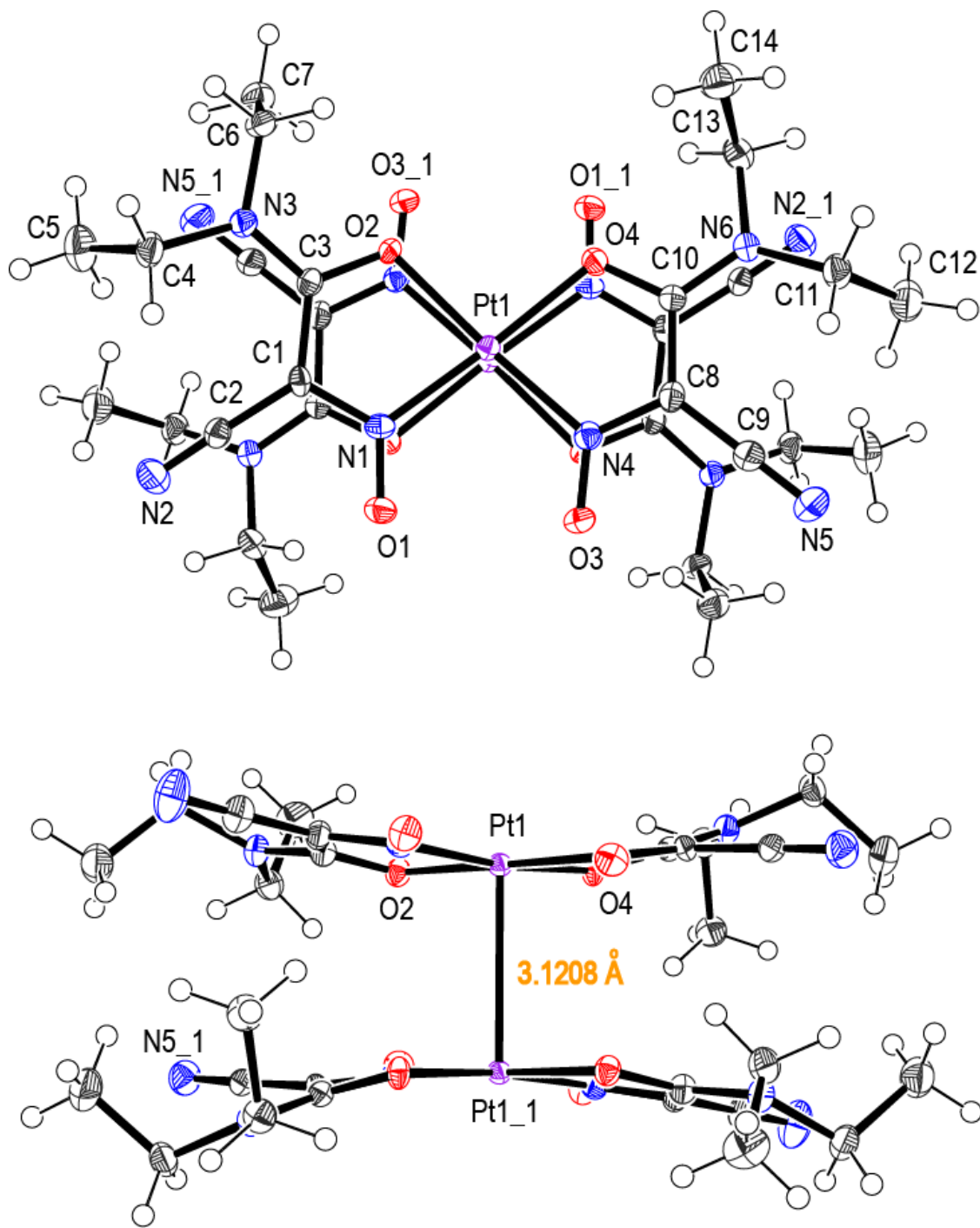


Figure 11. Top, side views and the numbering scheme in the structure of red, dimeric Pt(DECO)₂.

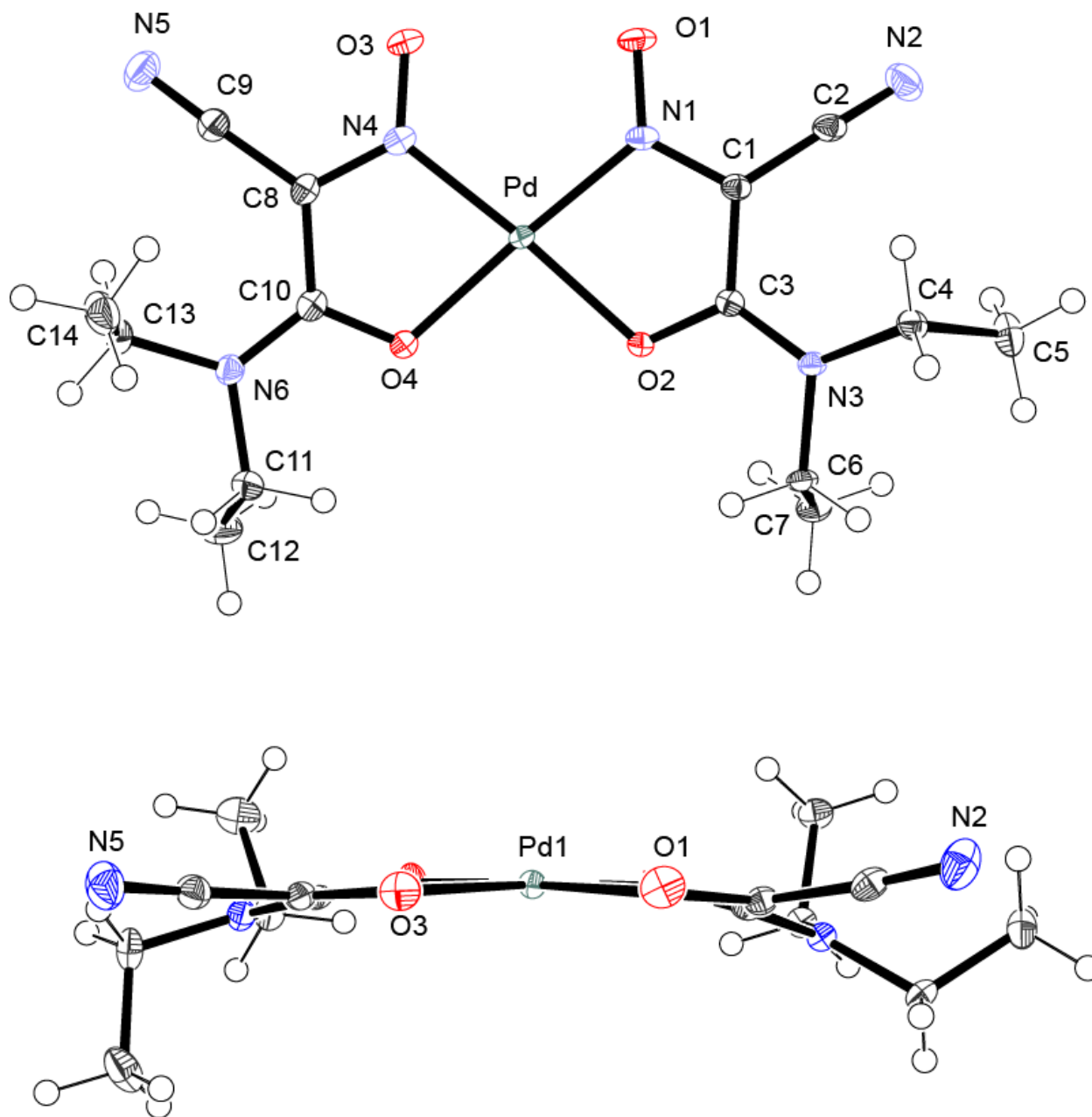


Figure 12. Top and side view in the structure of yellow Pd(DECO)₂; shown numbering scheme.

When crystallographic characterization of all suitable specimen was complete, a reasonable question rose: why dark-green Pt-DECO complex is having that color? The UV-visible spectrum of a very fine suspension of both Pd and Pt complexes evidenced presence of a broad low-energy “blue” band between 700 and 800 nm (Figure 13). This is the area typical of

mixed valence Pt-complexes. A suggestion has been made that in Danielle's dark-green polymer metal centers form "metal wires" due to metallophilic interactions. Thus, a "poker chip" type stack is formed. The mixed valence state can be formed by presence of a small quantities of Pt(III) or Pt(IV) centers, which can be generated either as the result of air (O₂) involvement, or as a products of disproportionation of Pt(II) centers to Pt(0) and the above lower oxidation states. The most interesting turned out to be recording of the emission spectrum from 1D polymeric Pt-DECO complex. Thus, excitation at 770 nm – where the maximum of absorbance is – lead to a very strong emission beyond 1000 nm (Figure 14)! That was a much unexpected finding!

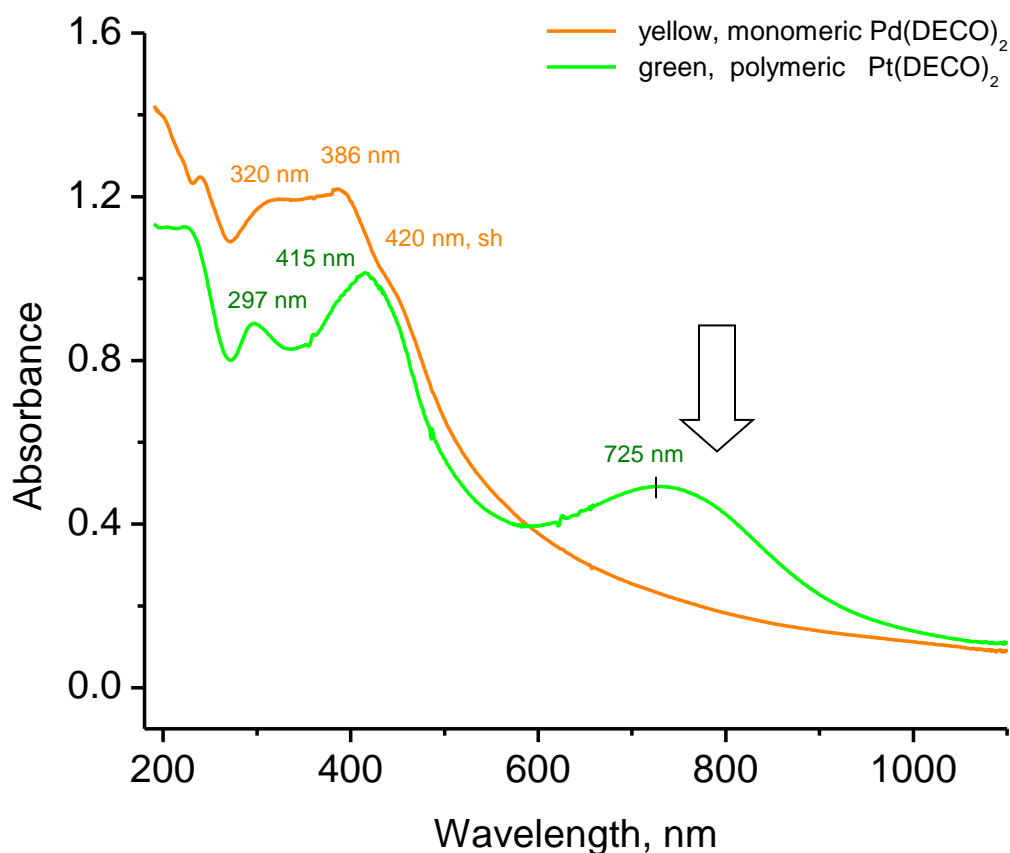


Figure 13. Comparison of solid state absorption spectra (recorded as fine suspensions in mineral oil) of 1D polymeric, dark-green Pt(DECO)₂ and yellow monomeric Pd(DECO)₂; T=+20°C. Color coded numbers indicate maxima in both spectra, while an arrow shows wavelength range (770 and 785 nm) used for the excitation during recording solid samples photoluminescence.

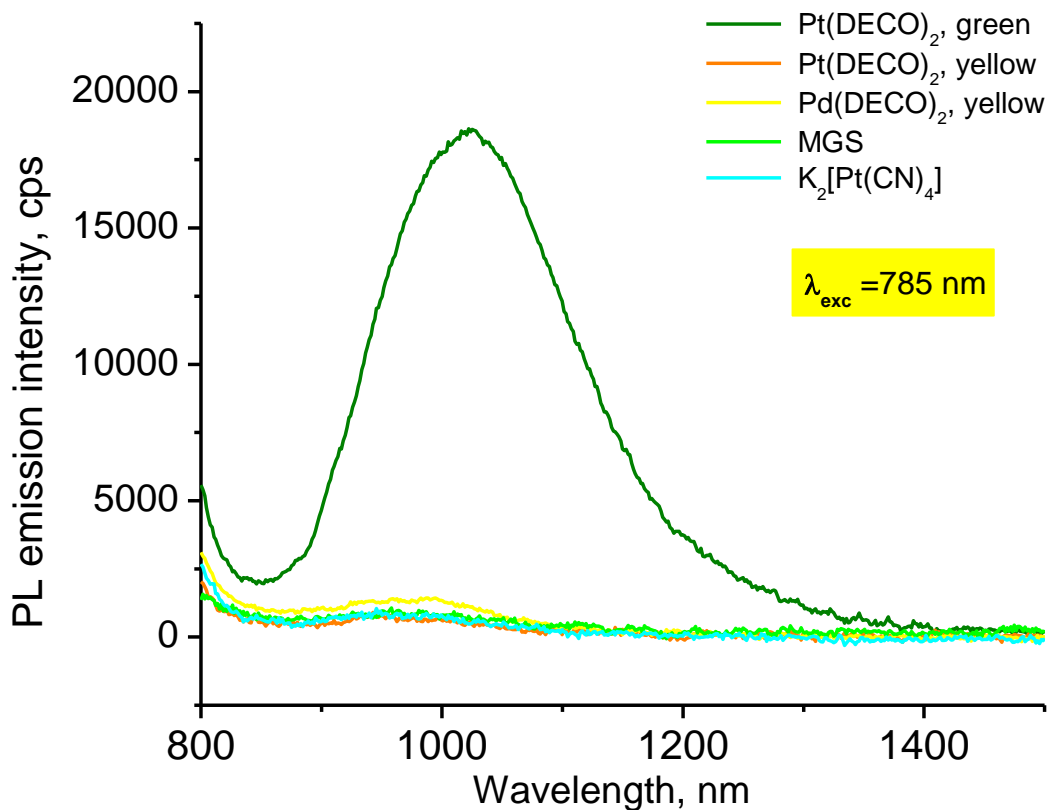


Figure 14. Emission spectrum of pellet of green 1D polymeric $\text{Pt}(\text{DECO})_2$ (~5 weight % in KBr), compared to emission profiles of yellow monomeric $\text{Pt}(\text{DECO})_2$, $\text{Pd}(\text{DECO})_2$, and standard 1D solids – Magnus' Green Salt (MGS) and $\text{K}_2[\text{Pt}(\text{CN})_4]$. Spectra recorded using CCD camera detector at $T=+20^\circ\text{C}$.

In summary, during Danielle Klaus' work we developed a unique supramolecular assembly based on the Pt(II) complex of PtL_2 composition (L = new cyanoxime ligand of the N-acetamides family, namely, 2-oximino-2-cyano-N,N'-diethylacetamide, HDECO). The complex has three polymorphic forms: monomeric yellow $\text{Pt}(\text{DECO})_2$, red dimeric $[\text{Pt}(\text{DECO})_2]_2$, and dark-green $[\text{Pt}(\text{DECO})_2]_n$. The latter complex represents a quasi-1D coordination polymer that strongly absorbs in the 400–900 nm range and luminesces at 1000–1200 nm. This compound also appears to be a solid solution containing nonstoichiometric amounts of Pt(IV) centers. Thus, aggregation of monomeric $\text{Pt}(\text{DECO})_2$ units into a stacked polymer in aqueous solution is driven

by metallophilic interactions and accompanied by the partial oxidation of Pt(II) to Pt(IV). Contrary to other previously reported unstable mixed-valence palladium or platinum based “metal wires”, presented in Danielle’s work dark-green polymeric platinum cyanoximate is stable in the solid state at room temperature for many months. This and similar NIR emissive platinum cyanoximate complexes can be used in light-emitting devices and optical sensors to cover wavelengths that are currently unavailable. In addition, because of the transparency of the biological tissue at 1060–1150 nm (second optical window) and established cytotoxicity of platinum cyanoximates the emissive platinum complexes can be utilized as theranostic agents for anticancer treatment and diagnostics.

Danielle Klaus’ work was very impressive and much appreciated. Unfortunately, she decided to change the research group and left my laboratory. Danielle joined the research group of Dr. Katie Fichter, biochemist, but in a few months was expelled from her research group. Then Ms. Klaus joined research group of Dr. Matthew Siebert – a computational chemist at the department – whom she left without thought MS degree. Sadly, having such a great synthetic chemist potential, she left Missouri State University with BS degree only.

One major peer-reviewed paper was published with Danielle being the first author!

Klaus, D.R., Keene, M., Silchenko, S., Berezin, M., Gerasimchuk, N. “1D Polymeric Platinum Cyanoximate: A Strategy toward Luminescence in the Near-Infrared Region beyond 1000 nm.” *Inorganic Chemistry*, **2015**, 54 (4), 1890-1900.

Conference presentation with Danielle Klaus:

48th Midwest Regional ACS Meeting (October 16-19, 2013; Springfield, MO)

D. R. Klaus,* M. Keene,* N. Gerasimchuk. “Synthesis, Spectra, and Crystal Structures of N,N’ diethylamide-2-cyano-2-oximino-acetamide and its Pt⁺² and Pd⁺² cyanoximates.” Abstracts, 48th Midwest Regional ACS Meeting, Springfield, MO. United States, October 16-19; MWRM-9.

49th Midwest Regional ACS Meeting (November 15-16, 2014; Columbia, MO)

Gerasimchuk, N.; Berezin, M.; Klaus, D.* “1D coordination polymers based on Pt(II) cyanoximates as new class of NIR emitters beyond 900 nm.” Oral presentation, #308.

Presentations of Danielle Klaus research at conferences and recognition of her achievements at the Annual Banquette:



Group tour to the middle of Missouri – Bridal Cave and Ha Ha Tonka State Park, July 2014



