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Ligand-Capped Silver Nanoparticles for the Tetection of Heavy Metal Ions

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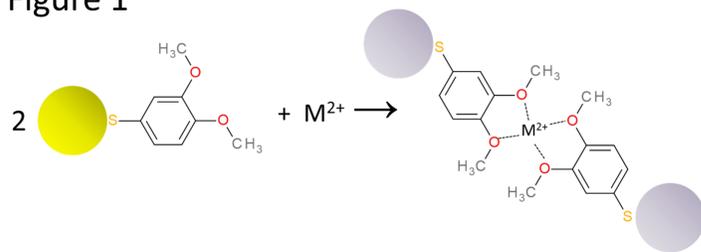
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Introduction

In the world today, pollution is a major problem. One important, yet hard to detect form of pollution is that of heavy metals in water systems.¹ These metals can come from the waste of manufacturing sites and consumer products. The most common of these metals are cadmium, chromium, copper, iron, lead, cobalt, manganese, mercury, nickel and zinc.¹ Recently, there has been research into the use of gold and silver nanoparticles (AuNP's and AgNP's respectively) to provide accurate and sensitive detection methods.^{2,3} One such study from researchers in China used AgNP's capped with the ligand 4-mercaptobenzoic acid to test the binding effects of metal ions. In the end they found their method was selective to copper and sensitive down to $2.5 \times 10^{-8} \text{M}$.³

The research presented in this report is studying the binding effects of the ligand 3,4-dimethoxybenzenethiol (DMBT) when attached to AgNP's. Once, the ligand is attached to the AgNP's through the sulfur atom, the Ag-DMBT nanoparticles bind with metal cations in a 2:1 ratio through the oxygens within the methoxy substituents as shown below. For the purposes of this study, the metal ions being tested were cobalt, nickel, copper, and lead.

Figure 1



Methods

Note: All glassware used is washed 3 times using Millipore water

Synthesis of Silver Nanoparticles (For 100mL)³

A 100mL stock solution of 1M silver nitrate is prepared using Millipore water. This stock solution is then used to make a 100mL solution of 10^{-4}M $\text{Ag}(\text{NO}_3)$. A stir bar is added and set to medium stirring. To this, 10mg of NaBH_4 is added and clear bright yellow solution of colloidal silver nanoparticles is formed.

Addition of DMBT Ligand³

After 5 minutes of stirring, 0.2mL of a 10^{-3}M solution of the DMBT ligand in Millipore water is added. The ligand is allowed to attach to the AgNP's on light to medium stirring for 30 minutes.

Metal Ion Test

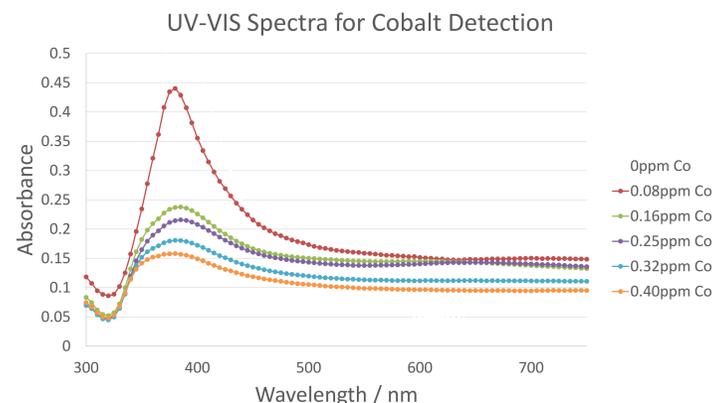
After 30 minutes, an appropriate amount of cleaned 10mL volumetric flasks are obtained and to them is added an appropriate amount of 20ppm metal ion stock solution is used to achieve the desired concentrations of 0, 0.08, 0.16, 0.25, 0.32, and 0.40ppm. The flasks are then filled to the mark with the AgNP-DMBT solution and allowed achieve color development for 2.5 hours.

Colorimetric Measurement

Once the Ag-DMBT nanoparticles have been given enough time to effectively bind with the metal ions, a UV-VIS spectrum from 300nm to 750nm is taken of the solutions using a Molecular Devices Spectramax M-series microplate reader.

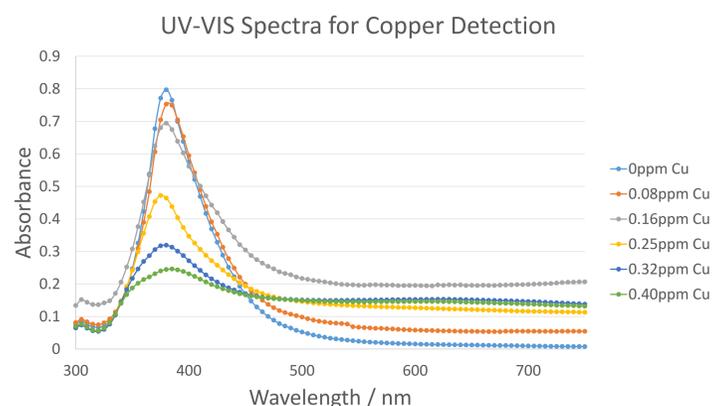
Results and Discussion

Graph 1



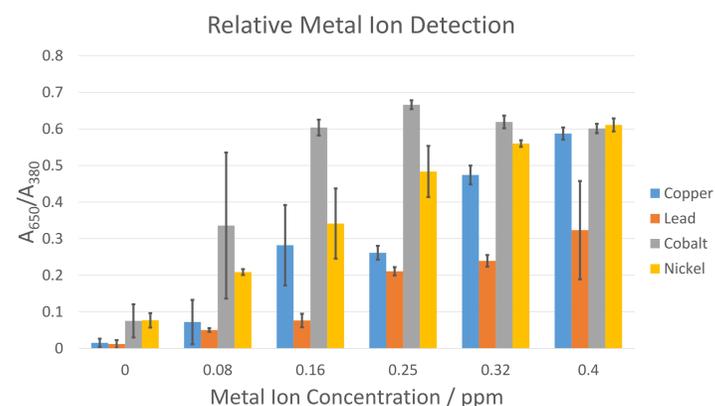
Shown above in Graph 1 are the UV-VIS spectra for the colorimetric binding of Co^{2+} with the DMBT ligand attached. Initially what can be seen in these spectra for a 0ppm concentration of Co^{2+} ions a peak absorbance found at 380nm. As the concentration of the Co^{2+} ions increase, the intensity of the absorbance at 380nm decreased while still remaining at or near the same wavelength. It can also be seen that as the ion concentration is increased there is a small wavelength shift towards the UV side of the spectrum. This possibly indicates that the particles are decreasing in size or are being destroyed. In Graph 2, a control run of just the nanoparticles without ligand and Co^{2+} ions is shown. It can be seen in this graph that at small concentrations of metal ions some intensity decrease and wavelength shift can be seen, but at larger concentrations (0.25 and 0.40ppm) there is distinct intensity change and shifting. With this control it can be inferred that cobalt is having a possible destructive impact on the particles themselves.

Graph 3

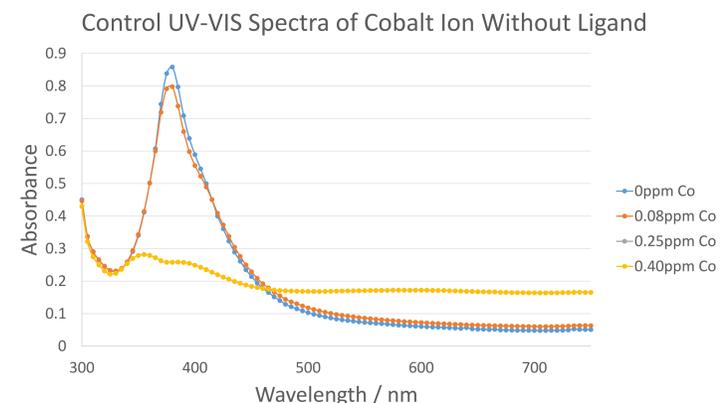


As with what was seen in Graph 1, a similar phenomenon can be observed in Graph 3 using Copper ions. Though similar, a clear difference can be seen in that the intensity shifting is evenly spaced as the concentration of the ions is increased. It is also seen that, as with the cobalt spectrum, there is a slight shifting in the λ_{max} . To test if the copper ion was possibly destroying the particles, a control run of the particles and the copper ions was carried out. The spectra of this control can be seen in Graph 4. It can be seen that though there is a slight wavelength shift in the peak absorbance, there is no drastic particle destruction or colorimetric differences as compared to what was seen with cobalt, and thusly binding may be occurring as hypothesized.

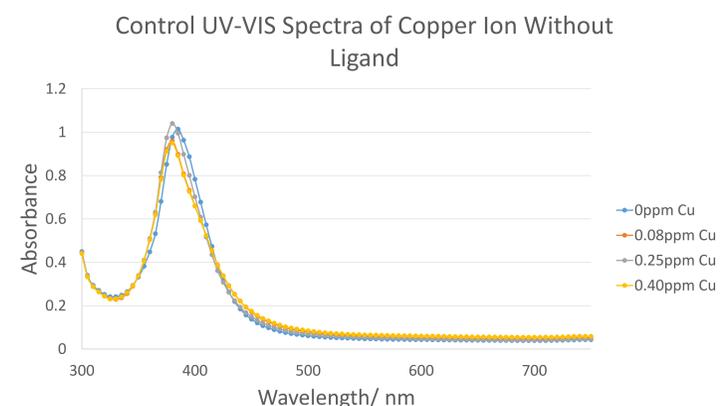
Graph 5



Graph 2



Graph 4



To the left, Graph 5 shows the absorbance ratio of copper, lead, cobalt, and nickel. The ratio used for this was the absorbance value at the wavelength of 650nm divided by that of the absorbance at a wavelength of 380nm. In general, it can be seen that there is a linear trend for the copper, nickel, and lead ions. It can also be seen that cobalt does not follow this trend. Using the trend seen in Graph 5 and the control test in Graph 2, another mechanism is indicated to explain this absorbance change for Co^{2+} . At this point, the reason for this absorbance change is unknown. Also, from Graph 5 it can be determined that Ni^{2+} and Cu^{2+} are binding to a higher degree than that of Pb^{2+} . This outcome is expected as Pb^{2+} is a softer lewis acid while Ni^{2+} and Cu^{2+} are harder acids and therefore more likely to bind to the relatively hard base of the DMBT ligand.⁴

Conclusion

In conclusion, the detection tests of Co^{2+} ions were observed to be outliers when compared to control tests. Based on the comparison to a control test (Graph 2) and the relative binding ratios (Graph 5), it is hypothesized that cobalt is playing a destructive role in the nanoparticle-ligand system. The extent of this possible role is unknown at this time.

The other metal ions (Pb^{2+} , Ni^{2+} , and Cu^{2+}) when compared to a control test, behaved as expected according to Figure 1. Though the particles behaved as expected a distinct peak at a higher wavelength does not appear. This suggests a possible higher order aggregation system that is forming as the Ag-DMBT particles bind.

Lastly, Ni^{2+} and Cu^{2+} appear to be binding at a higher degree than the Pb^{2+} . This is attributed to the idea that Pb^{2+} is a softer lewis acid than the Ni^{2+} and Cu^{2+} and therefore more incompatible to bind to the relatively hard lewis base that is the DMBT ligand.

Future Work

- Test more transition metal ions (M^{2+} , M^{3+})
- Characterize the AgNP-DMBT nanoparticles using ^1H NMR and IR spectroscopy to provide evidence of ligand binding to the AgNP's.
- Obtain TEM images of the nanoparticles and calculate if enough ligand solution is being added as well as show possible aggregation and particle destruction
- Investigate the use of mixed ligand systems to provide particle protection and binding.

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