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Mechanism Analysis of Copper (II) Ions Interacting with Dimethylaminocyanostilbene

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Mechanism analysis of copper(II) ions interacting with dimethylaminocyanostilbene

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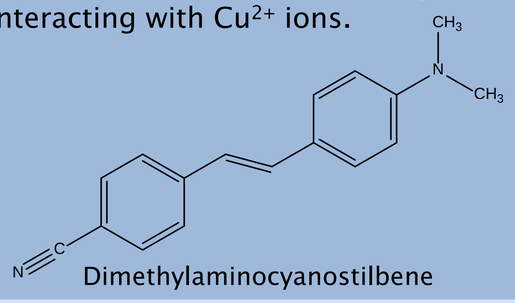
Abstract

Previous research has suggested that the fluorescence of dimethylaminocyanostilbene (DCS) is selectively quenched by copper(II) ions.[1] This study aimed to elucidate the fluorescence quenching mechanism and to explore its potential application to screen for copper ions in water samples. A spectroscopic Job Plot analysis was used to determine the stoichiometric ratio of DCS–copper(II) ion binding.[2] Additionally, DCS was mixed with various buffered metal ion solutions and tested in different pH environments to reveal any ion-dependent and/or pH-dependent fluorescence response. Nuclear magnetic resonance spectroscopy (NMR) analysis of DCS mixed with various amounts of buffered copper(II) solution was also performed to further study the interaction between copper(II) ions and DCS.

Introduction

Prior works has shown that dimethylaminocyano-stilbene (DCS) exhibits a useful fluorescence behavior under UV light by turning off (being quenched) in the presence of Cu^{2+}, Al^{3+}, and Fe^{3+} ions but not other metal ions, including Hg^{2+}, Mn^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, and Ca^{2+} ions. The interaction of DCS with copper(II) ions is of particular interest because of the biological and environmental importance of copper and because of the potential commercial application of a sensor that can detect EPA-actionable levels of copper in water (1.3 ppm/20.5 μM). Why and how the quenching observed in previous studies occurs has not been elucidated. This study investigates how DCS may be interacting with Cu^{2+} ions.



Dimethylaminocyanostilbene

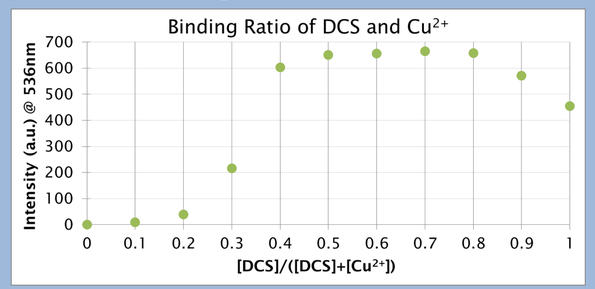
Methodology

- For Job Plot analysis, spectroscopy data of DCS and Cu^{2+} mixtures of a range of mole ratios were collected while the total concentration was kept constant at 51.3 μM.
- Nitrate and chloride salts were used to prepare various 2 mM metal ion solutions in a HEPES buffer (pH 7). DCS was mixed with each solution and spectroscopy data was collected.
- Fluorescence response of DCS was measured as buffered (pH 7) 2 mM Cu^{2+} solution was added.
- Fluorescence of DCS mixed with Cu^{2+} solutions and DCS mixed with deionized (DI) water solutions were measured at various pH levels.
- DCS solution was titrated with Cu^{2+} solution and NMR analysis was run after each addition.

* A Cary Eclipse spectrometer was used for all spectroscopy.

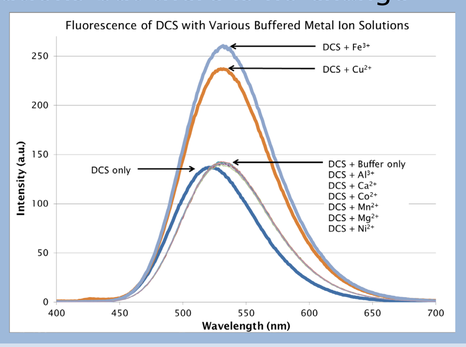
Results

- The Job Plot does not show a clear peak that would indicate the binding ratio.



- Fluorescence output of DCS is higher when mixed with Cu^{2} or Fe^{3+} solutions but there is no change with other ions.

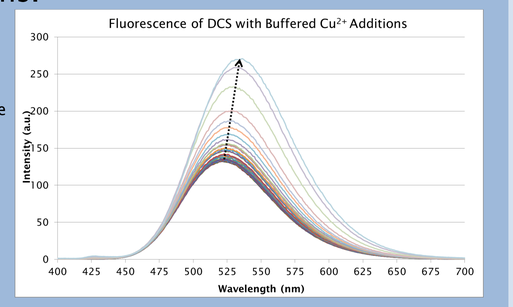
3.5 mL of 9.3 μM DCS in acetonitrile was mixed with .5 mL 2 mM metal ion aqueous buffered solution.



Results (cont'd)

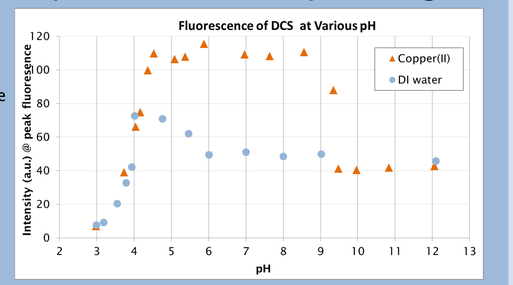
- When using buffered Cu^{2+} solution, the fluorescence gradually increases with increasing copper(II) additions.

3 mL of 9.3 μM DCS in acetonitrile was mixed with 0 μL to 800 μL total addition of pH 7, buffered 2 mM Cu^{2+} aqueous solution.



- In both copper(II) solutions and in DI water, the fluorescence intensity of DCS varies as pH changes.

3 mL of 8.7 μM DCS in acetonitrile was mixed with .5 mL 2 mM copper(II) solution. 9.3 μM DCS solution was used with DI water.



Conclusion

- Quenching of DCS was not seen with *buffered* copper(II) solution in contrast to previous studies which did not use buffered solution.
- Results suggest fluorescence intensity of DCS is a function of pH, not due to interaction with metal ions as previously thought.
- NMR data also supports this conclusion; no 1:1 binding effect was observed.
- Fe^{3+}, Al^{3+}, and Cu^{2+} are known to be acidic cations. These ions are good Bronsted-Lowry and Lewis acids.
- Future work includes determining the fluorescence quantum yield of DCS and investigating DCS analogs such as an amidine based chemosensor that may work as a copper and iron sensor (as suggested by Nandre, et al).[3]

Bibliography

1. Stephen Gilbert, Erica Evans, Dr. Ryan Hayes, Dr. Desmond Murray. Investigation into the mechanism of copper(II) ions sensing using dimethylaminocyanostilbene fluorescence.
2. MacCarthy, Patrick. Simplified Experimental Route for Obtaining Job's Curves. *Analytical Chemistry.* December 1978, 50, 14, 2165.
3. Nandre, Jitendra; Patil, Prashant; Sahoo, Suban; Redshaw, Carl; Mahulikar, Pramod; Patil, Umesh. The Amidine Based Colorimetric Sensor for Fe^{3+}, Fe^{2+}, and Cu^{2+} in Aqueous Medium. *Journal of Fluorescence.* November 2014, 24, 6, 1563-1570.