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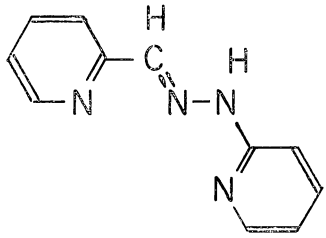
Formation Constants of the Copper(II) Compounds of Pyridylalpyridylhydrazine

L. Keith Hunt and Harvey Diehl

Abstract. Bivalent copper and the Schiff's base pyridylalpydidylhydrazine form two compounds, composed respectively of one molecule and of two molecules of the organic compound to one atom of copper, and having ultra violet absorption spectra differing only in the value of the molar extinction coefficients at the absorption maxima, 15,100 and 22,450, respectively at 345 mμ. The respective formation constants are 2.4 x 10^5 and 2.8 x 10^5 as determined from spectrophotometric data, the method used being unusual in that the ultra violet absorption data provided a direct measure of the free ligand present.

Hunt and Diehl (1, 2, 3) have shown that pyridylalpridylhydrazine (1,3-bis(2'-pyridyl)-2,3-diaza-1-propene), the Schiff's



base of 2-pyridylcarboxaldehyde and 2-pyridylhydrazine, is a useful reagent for the spectrophotometric determination of small amounts of cobalt in the presence of iron, nickel, copper, and other bivalent transition elements which can be extracted into nonpolar solvents. The cobalt(III)-PDP compound is not extracted. The separation of the other transition elements from cobalt is clean, and the cobalt remains quantitatively in the water layer as one of the most intensely colored of all metal compounds known. In the course of the work, attention was directed toward learning the nature of the iron, nickel and copper compounds. The copper compounds described first by Lions and Martin (4) and by Geldard and Lions (5) proved of interest because, as shown in the present work, the formation constants for the attachment of the second molecule of PDP to the copper atom is greater than that for the first. In this paper we describe the method of measurement used for the determination of these constants.

Experimental Work

Apparatus and Materials. Absorption spectra were obtained on a Beckman DU spectrophotometer using 1-cm quartz cells.

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All pH measurements were made with a Beckman Model G pH meter standardized against standerd buffers. The constant ionic strength buffers used in all solutions in spectrophotometric studies were prepared following the directions of Bates (6).

Additions of small volumes of reagents were made using a syringe microburet, model SB2 manufactured by the Micro-Metric Instrument Company, Cleveland, Ohio.

Standard solutions of copper(II) were prepared by dissolving pure copper wire in dilute nitric acid. The standard solution was 1.000×10^{-3} M in copper.

1,3-Bis(2′-pyridyl)-2,3-diaza-1-propene (PDP) was prepared by the procedure described in an earlier communication (1). Standard solutions were prepared by weight. The compound was dissolved in 95 per cent ethanol and diluted to mark with ethanol.

Reaction of Copper and PDP. Absorption Spectrum. The spectrum of the copper compound was measured in a solution of pH 8.45, $\mu = 0.1$. The solution was prepared by addition of excess PDP to a given amount of copper(II) and diluting to a known volume with the pH 8.45 buffer. The absorbance of the PDP alone in buffered solutions of the same pH was also measured. The absorption spectra are shown in Figure 1.

The change in the absorption spectrum of the copper-PDP system was studied as a function of the ratio of copper to PDP in solution. To each of eight 25-ml. volumetric flasks was added 0.1 ml. of 1.00×10^{-2} M PDP. Varying amounts of 1.00×10^{-3} M copper(II) solution were added. The solutions were then diluted with pH 8.45 buffer. Absorbance was then measured at 440 mμ and 345 mμ.

Combining Ratio. The combining ratio of copper to PDP in aqueous buffered solutions was investigated by the mole-ratio method of Yoe and Jones (7). To each of five 50-ml. volumetric flasks was added 0.1 ml. of 1.00×10^{-2} M PDP by syringe/microburet. Varying amounts of the standard 1.00×10^{-3} M copper (II) solution were then added. The solutions were diluted with pH 8.45 buffer and the absorbance of each measured at 440 mμ. A similar experiment was carried out in which a constant amount of copper(II) was taken and the volume of 1.00×10^{-2} M PDP varied.

Results

As will be seen from Figure 1, the maximum absorbance of the cupric-PDP compound falls at 440 mμ in the visible region of the spectrum. The absorption peak is very broad, and the molar extinction coefficient of 20,000 1 cm^{-1} $mole^{-1}$ is very large for a copper compound.

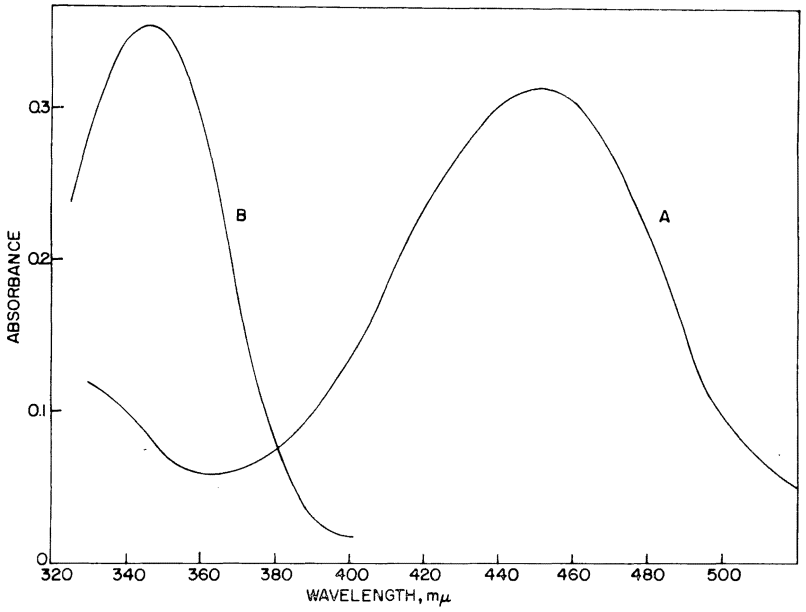

Figure 1. Absorption Spectra of Cu(II) -PDP and PDP
A. 4.00 x 10^{-5}M Cu(II), 2.00 x 10^{-5} M PDP in 0.1 M sodium tetraborate
B. 2.00 x 10^{-5} M PDP in 0.1 M sodium tetraborate

The data in Table 1 shows that the peak at 345 mμ is proportional to the unbound or free PDP concentration. As the 440 mμ peak increases due to increase in the amount of the copper-PDP compounds in solution, the peak at 345 mμ decreases in proportion. Thus, the absorbance of the 345 mμ peak is a direct measure of free PDP concentration. The copper-PDP compound apparently does not have significant absorbance in this region. The 345 mμ peak of the free PDP and the 440 mμ peak of the copper compounds are shown in Figure 1.

Table 1. Change in the Absorption Spectrum of the Copper-PDP System with Varying Copper Concentration and Constant PDP Concentration

[Cu] x 10^6	Absorbance	
	345 mμ	440 mμ
0.80	0.699	0.171
1.20	0.606	0.245
2.00	0.485	0.407
1.55	0.331	0.513
1.02	0.313	0.642

The mole-ratio plots showed that either the 2:1 or the 1:1 PDP to copper compound is formed in solution depending on the ratio of copper (II) to PDP. Both species are probably present in solution to a measurable extent. Both compounds

appear to have maximum absorbance in the visible region of the spectrum at about the same wave length.

Calculation of the Formation Constants. Since the absorption of the 345 mμ peak is a direct measure of the free PDP concentration and the total concentrations of both PDP and copper (II) are known, the n̄ function of Bjerrum (8) can be calculated and the formation constants of the copper-PDP compounds calculated. The graph of n̄ versus p(PDP) is shown in Fig. 2,

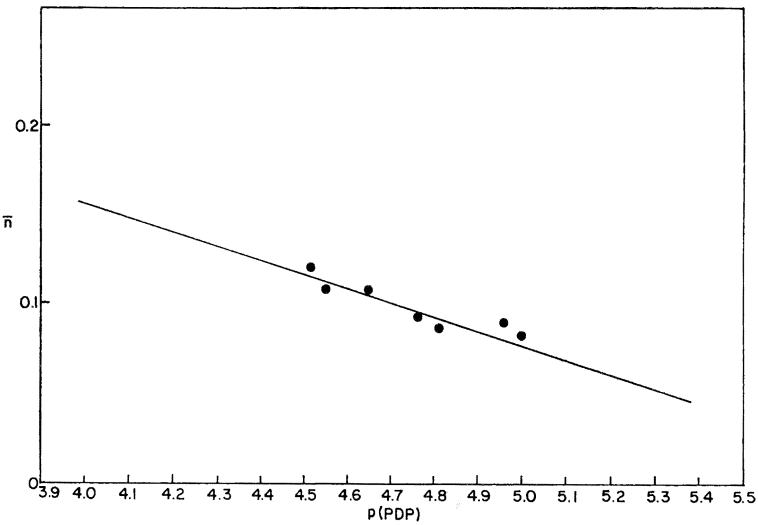

Figure 2. n̄ Verse p(PDP) for Solutions Containing Copper and PDP

p(PDP) being the negative logarithm of the concentration of PDP. Preliminary values of k_1 and k_2 were obtained from the graph at n̄ equal to 0.5 and 1.5 where $k_1 = 1/(PDP)$ and $k_2 = 1/(PDP)$ respectively. Using the values of the molar extinction coefficients ε_1 and ε_2 measured in the mole-ratio study, the preliminary values of the formation constants were then refined by successive approximation. The values obtained are $\varepsilon_1 = 15{,}104$ lcm^{-1} mole^{-1}, $\varepsilon_2 = 22{,}450$ lcm^{-1} mole^{-1}, $\beta_1 = 2.385 \times 10^5$, and $\beta_2 = 6.693 \times 10^{10}$. From the over-all formation constants, k_1 and k_2 are 2.4×10^5 and 2.8×10^5, respectively.

Discussion

Lions and co-workers (9) reported the formation constant for the 1:1 copper to PDP compound in strong acid solution as 4×10^{11}. They reported that no evidence could be found for the formation of a higher species. The fact that the formation constants by Lions were measured in very acid solutions (pH 1.5)

probably explains their failure to detect a 2:1 compound. With large formation constants such as those for PDP and copper, union may be very nearly complete at acid pH values, and pH titration methods are not the most reliable techniques. Other workers have criticized the determination of formation constants in such acid solutions (10). The mole-ratio studies reported in this paper show that both the 2:1 and the 1:1 compounds are formed.

Although compounds similar to the copper-PDP compounds with k_2 greater than k_1 are uncommon, a few such compounds are known (10, 11, 12). The 1:1 copper-PDP compound is probably planar, and bounding is by dsp^2 hybrid orbitals. Both the 1:1 and the 2:1 copper compounds are paramagnetic (5, 9). Consideration of molecular models shows that the second PDP molecule must coordinate copper at right angles to the first PDP molocule. Steric hindrance will not permit the formation of a 2:1 planar compound. It is obvious that two pyridine nitrogen atoms of each PDP molecule alone cannot be coordinated to the copper since this would involve formation of an eight-membered ring. Such rings are known to be unstable. Steric hindrances would also prevent the formation of a planar 2:1 copper compound with only two of the nitrogen atoms of each ligand. Copper must be coordinated to three nitrogens of each PDP molecule to form a hexacoordinated species. Hexacoordinated copper is known for other unsaturated aromatic amines, and Irving and Mellor (11) report that 2,9-dimethyl-l, 10-phenanthroline forms a compound with copper in which k_2 is greater than k_1. They suggest that repulsion between the first ligand molecule and the water shell around the molecule facilitates entry of the second ligand molecule in a plane at right angles to itself so that k_2 is greater than k_1. James and Williams (12) suggest that π-bonding involving the filled d_ϵ-orbitals of copper and an empty molecular orbital of the ligand allows copper(II) to coordinate three bipyridine molecules. Since bipyridine and other unsaturated aromatic amines are known to be good electron acceptors (14), π-bonding arising from mixing of the filled d_ϵ level of copper(II) and an empty π^*-molecular orbital on the PDP molecule would give a very stable compound. The π-molecular orbital of such a system covers the whole π-system of the ligand and the metal ion (15). Such π-bonding would explain the unusual stability of the 2:1 compound in basic aqueous solution.

ACKNOWLEDGEMENT

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Can Chromatography Occur in Nature?

PAUL J. KEMP AND HARVEY DIEHL

Abstract. Adsorption of calcium and magnesium on a sandstone from a bicarbonate solution has been demonstrated. On elution with water saturated with carbon dioxide, the magnesium passes off first. The chromatographic separation of magnesium from calcium can thus occur under conditions which can prevail in nature.

We ask: Does chromatography play a part in geochemistry? More specifically we ask: Can calcium and magnesium be separated by the chromatographic process on sandstone? Even more specifically: Can such a separation be demonstrated in the laboratory on a natural sandstone under conditions which can occur in nature? The answers to all three questions appear to be yes.

For the demonstration we selected sandstone from the Chugwater and Tensleep formations of north central Wyoming. A

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