



Spectrum–structure correlation for visible absorption spectra of copper(II) complexes showing axial co-ordination in aqueous solution

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Abstract

We attempted to draw some general considerations regarding the ability of the visible absorption spectra to provide information on axial co-ordination around copper(II) ion in aqueous solution. A series of visible spectra was recorded on the copper(II)–2,2′-bipyridine and copper(II)–L-aspartic acid systems. 2,2′-Bipyridine is known for its ability to co-ordinate copper(II) in axial position(s) as well, while L-aspartic acid is a potential tridentate ligand whose ability to chelate in axial position has been here investigated.

Combined pH-metric and visible absorption spectrophotometric measurements were performed; visible absorption spectra were recorded during alkalimetric titrations as a function of pH. Further computer-assisted treatment allowed obtaining absorption spectra of single complexes. A series of axially co-ordinated copper(II) complexes found in the literature was also considered. Structural assignment of planar complexes is based on an empirical equation previously published by our research group, which allows an estimation of the ligand field strength of the equatorial donor groups involved. This equation can now help to strengthen the discussion and to assess a criterion to establish the axial co-ordination mode of copper(II) ion. The location of a donor group along the z-axis of the copper(II) distorted octahedron causes a red shift in the absorption spectrum. A quantitative estimation of the red shift per donor group was performed and ranges of red shifts for single donor groups were identified: we calculated a mean value of 36 nm, while extreme values are 19 and 58 nm.

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Keywords: Visible absorption spectra; Molecular spectrophotometry; Copper(II) ion; Axial co-ordination; Red shift; Complex formation; Spectrum–structure correlation

1. Introduction

This paper inserts itself in a project of ours devoted to a careful investigation on spectrum–structure correlation for copper(II) complexes in aqueous solution based on visible absorption spectrophotometry. The work has been subdivided into three papers. Previous papers dealt with: (i) the assessment of an equation for the estimation of λ_{max} value for equatorial co-ordinated complexes, by means of the individual contribution optimization of the most common donor groups to the overall ligand field strength of a complex in solution [1] and (ii) the relationship between

λ_{max} and ϵ_{max} values of equatorial co-ordinated copper(II) complexes in solution [2].

Axial co-ordination represents a serious obstacle to the reliability of the structural assessment process for copper(II) complexes in solution, being the Jahn–Teller effect [3] the cause of the well known distorted octahedral geometry of co-ordination in this cation. Very often, when dealing with copper(II) co-ordination compounds in solution, the substitution of water molecules of the aqua-ion $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ [4] by donor groups starts from the four positions of the equatorial plane of the distorted octahedron and, successively, the two apical positions – along the usually marked “z-axis” – are involved. The former situation has been treated in [1]. The latter situation is now under further attempt of rationalization. In our opinion, no real change in geometry is observed if donor groups occupy

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Table of Contents Spectra Structure Correlation

1. Understanding the eBook Spectra Structure Correlation
 - The Rise of Digital Reading Spectra Structure Correlation
 - Advantages of eBooks Over Traditional Books
2. Identifying Spectra Structure Correlation
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Spectra Structure Correlation
 - User-Friendly Interface
4. Exploring eBook Recommendations from Spectra Structure Correlation
 - Personalized Recommendations
 - Spectra Structure Correlation User Reviews and Ratings
 - Spectra Structure Correlation and Bestseller Lists
5. Accessing Spectra Structure Correlation Free and Paid eBooks
 - Spectra Structure Correlation Public Domain eBooks
 - Spectra Structure Correlation eBook Subscription Services
 - Spectra Structure Correlation Budget-Friendly Options

6. Navigating Spectra Structure Correlation eBook Formats
 - ePub, PDF, MOBI, and More
 - Spectra Structure Correlation Compatibility with Devices
 - Spectra Structure Correlation Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Spectra Structure Correlation
 - Highlighting and Note-Taking Spectra Structure Correlation
 - Interactive Elements Spectra Structure Correlation
8. Staying Engaged with Spectra Structure Correlation
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Spectra Structure Correlation
9. Balancing eBooks and Physical Books Spectra Structure Correlation
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Spectra Structure Correlation
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
11. Cultivating a Reading Routine Spectra Structure Correlation
 - Setting Reading Goals Spectra Structure Correlation
 - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Spectra Structure Correlation
 - Fact-Checking eBook Content of Spectra Structure Correlation
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
 - Integration of Multimedia Elements

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