



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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Spectra Structure Correlation

John Perrow Phillips



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Spectra-structure Correlation John Perrow Phillips, 1966 **Infrared and Raman Spectroscopy** Peter Larkin, 2017-11-13 Infrared and Raman Spectroscopy Principles and Spectral Interpretation Second Edition provides a solid introduction to vibrational spectroscopy with an emphasis on developing critical interpretation skills This book fully integrates the use of both IR and Raman spectroscopy as spectral interpretation tools enabling the user to utilize the strength of both techniques while also recognizing their weaknesses This second edition more than doubles the amount of interpreted IR and Raman spectra standards and spectral unknowns The chapter on characteristic group frequencies is expanded to include increased discussions of sulphur and phosphorus organics aromatic and heteroaromatics as well as inorganic compounds New topics include a discussion of crystal lattice vibrations low frequency THz confocal Raman microscopy spatial resolution in IR and Raman microscopy as well as criteria for selecting Raman excitation wavelengths These additions accommodate the growing use of vibrational spectroscopy for process analytical monitoring nanomaterial investigations and structural and identity determinations to an increasing user base in both industry and academia Integrates discussion of IR and Raman spectra Pairs generalized IR and Raman spectra of functional groups with tables and text Includes over 150 fully interpreted high quality IR and Raman reference spectra Contains fifty four unknown IR and Raman spectra with a corresponding answer key Spectra-Structure Correlation John P. Phillips, 2013-10-22 Spectra Structure Correlation focuses on absorption spectroscopy of organic compounds including radiation absorption and analysis of compounds The publication first offers information on wavelength classification of absorption spectra intensities and shapes of absorption bands mechanisms for the absorption of radiation and solvent phase and temperature effects The text also focuses on the spectra of hydrocarbons as well as olefins cyclopropanes benzenes allenes and cumulenes cyclobutanes cyclopentanes and cyclohexanes The manuscript reviews compounds with oxygen and nitrogen functions Discussions focus on aldehydes and ketones alcohols carboxylic acids phenols ethers and peroxides acid derivatives amides and imides amines and nitriles and related functions The text also ponders on organic compounds containing halogen sulfur phosphorus silicon or boron inorganic compounds and complex materials Concerns include polymers steroids purines pyrimidines nucleic acids amino acids polypeptides and proteins The publication is a dependable reference for readers interested in absorption spectroscopy or organic compounds **UV Spectroscopy** B.J. Clark, T. Frost, M.A. Russell, 1993-04-30 This book is intended as an introductory text It starts at the very fundamentals of the interaction of light and matter and progresses through the laws of light absorption instrumentation and standards to the newer chemometric techniques Other chapters cover colour structural aspects of UV spectroscopy detection in high performance liquid chromatography and fluorescence

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Metal Organic Frameworks as Heterogeneous Catalysts Fransesc Llabres i Xamena, Jorge Gascon, 2013-07-01 Catalysis has always been part of the development of mankind from the fermentation of alcoholic drinks through the development of fertilisers in the agricultural revolution and production of bulk chemicals in the 20th Century Today society demands improved production routes with greater product output and energy efficiency the ultimate goal to achieving this would be having all catalytic reactions in concert effectively functioning like a biological cell Metal organic frameworks MOFs are a relatively new type of hybrid material Their crystalline porous structure built up from organic and inorganic building blocks presents a vast array of composition porosity and functionality offering enormous potential in catalytic systems This book examines the latest research and discovery in the use of MOFs in catalysis highlighting the extent to which these materials have been embraced by the community Beyond presenting a digest of recent research by major players in the field the book presents the strategies behind recent developments providing a lasting reference for seasoned researchers and newcomers to the field

Advances in Near Infrared Spectroscopy and Related Computational Methods Christian Huck, Krzysztof B. Boc, 2020-01-03 In the last few decades near infrared NIR spectroscopy has distinguished itself as one of the most rapidly advancing spectroscopic techniques Mainly known as an analytical tool useful for sample characterization and content quantification NIR spectroscopy is essential in various other fields e g NIR imaging techniques in biophotonics medical applications or used for characterization of food products Its contribution in basic science and physical chemistry should be noted as well e g in exploration of the nature of molecular vibrations or intermolecular interactions One of the current development trends involves the miniaturization and simplification of instrumentation creating prospects for the spread of NIR spectrometers at a consumer level in the form of smartphone attachments a breakthrough not yet accomplished by any other analytical technique A growing diversity in the related methods and applications has led to a dispersion of these contributions among disparate scientific communities The aim of this Special Issue was to bring together the communities that may perceive NIR spectroscopy from different perspectives It resulted in 30 contributions presenting the latest advances in the methodologies essential in near infrared spectroscopy in a variety of applications

Near-Infrared Spectroscopy Yukihiro Ozaki, Christian Huck, Satoru Tsuchikawa, Søren Balling Engelsen, 2020-11-13 This book provides knowledge of the basic theory spectral analysis methods chemometrics instrumentation and applications of near infrared NIR spectroscopy not as a handbook but rather as a sourcebook of NIR spectroscopy Thus some emphasis is placed on the description of basic knowledge that is important in learning and using NIR spectroscopy The book also deals with applications for a variety of research fields that are very useful for a wide range

of readers from graduate students to scientists and engineers in both academia and industry For readers who are novices in NIR spectroscopy this book provides a good introduction and for those who already are familiar with the field it affords an excellent means of strengthening their knowledge about NIR spectroscopy and keeping abreast of recent developments

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