

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

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Received 9 January 2006; accepted 5 April 2006

Available online 8 May 2006

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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