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On the structure of transition metals complexes with the new tridentate dye of thiazole series: Theoretical and experimental studies

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ABSTRACT

The 1-[(5-Benzyl-1,3-thiazol-2-yl)diazenyl]naphthalene-2-ol (BnTAN) is a recently synthesized azo dye that can act as a tridentate ligand in complexes with transition metals. In a series of previous works, this analytical reagent was shown to be applicable for selective, reliable, express and relatively inexpensive determination of heavy metals in different objects through the spectrophotometric technique. Although the action of 1-(2-thiazolylazo)-2-naphthol (TAN) dyes as tridentate ligands has been suggested in the literature long time ago, due to the lack of experimental data, it was necessary to investigate the mechanism of formation and the structure of BnTAN complexes with the such transition metals as Cu(II), Zn(II) and Cd(II). Furthermore, the reactivity and properties of different acidity forms and conformers of BnTAN and related TAN dyes were not fully defined, so the determination of these properties by analysis of wavefunction was also necessary.

Two standard spectrophotometric methods and voltammetric technique were used to determine the composition of complex of BnTAN with metals ions. All three experimental methods indicate that coordination ratio of metal:dye is equal to 1:2. Moreover, this study reports the stability and geometry of conformers of different forms (anionic/neutral/cationic) of BnTAN, along with a detailed analysis of electronic properties, reactivity and aromaticity of the most stable conformers of BnTAN forms. Each of the above forms has some difference in position of benzyl ring against the thiazole moiety, which is explained in terms of attraction and repulsion of these two fragments induced by partial atomic charges. The crucial influence of hydrogen bond and weak non-covalent interactions between naphthyl, aza- and thiazolyl fragments has been established.

The quantum chemical calculations have shown that partial atomic charges of anionic, neutral and cationic forms can explain the reactivity of each BnTAN form, and have also clarified the mechanism of formation of metal complex through the connection of metal with phenol oxygen, thiazolyl nitrogen and one nitrogen of aza group – thus giving two five-membered metal-containing cycles and confirming that BnTAN acts as a tridentate ligand.

The obtained results introduce novel and crucial information which can assist in understanding the mechanism of complex formation of BnTAN and display the strength and level of detail of applying quantum chemical methods to reveal the reactivity, energy properties, and electronic properties of this new dye.

1. Introduction

The use of thiazolylazo dyes in the industry and everyday's life has great advantages due to the wide spectrum of colors and relatively low prices [1]. Thiazolylazo dyes with naphthyl moiety are widely used in the chromatographic columns [2,3], in data

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