Synthesis, structure, UV-visible spectrum, and formation constant of bis (3-amino-1-phenyl-2-buten-1-onato) copper (II) and comparison with bis (4-aminopent-3-en-2-onato) copper (II)

Mina Jamialahmadi, Sayyed Faramarz Tayyari, Mohammad Vakili, Ali Reza Berenji*

Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 91779, Iran

Recently, there have been many reports on the late transition metal complexes as catalysts for olefin homo- and copolymerization [1-3]. Bao et al. [4] have been investigated on a series of copper (II) complexes of β-ketoamine ligands for polymerization of olefins. According to Gurr's study [5], the unit cells of bis (4-aminopent-3-en-2-onato) copper (II), Cu(APO)$_2$, and bis (3-amino-1-phenyl-2-buten-1-onato) copper (II), Cu(APBO)$_2$, are orthorhombic and monoclinic, respectively.

In this work, we have given the modified synthesis, X-ray crystallography information, and calculated formation constants of Cu(APBO)$_2$ by means of density functional theory (DFT) studies and have compared with those observed experimentally. The results also compared with Cu(APO)$_2$ [6].

The results show that the single crystal of Cu(APBO)$_2$ is more regular than Cu(APO)$_2$ (Figs. 1 and 2) and crystallographic and DFT calculation data of Cu(APBO)$_2$ are closer to each other than those of Cu(APO)$_2$.

UV-vis. spectrum of Cu(APBO)$_2$ indicates λ_{max} at 580 nm related to $\Delta E_{elect} = 206$ kJ mole^{-1}; however, these values for Cu(APO)$_2$ are 567 nm and 211 kJ mole^{-1}, respectively. In DFT calculations, ΔE_{elect} was considered as the difference between HOMO and LUMO orbitals and obtained 400 and 459 kJ mole^{-1} for Cu(APBO)$_2$ and Cu(APO)$_2$, respectively. Π-delocalization of electrons in Cu(APBO)$_2$ is responsible for the less difference between HOMO and LUMO energy levels.

According to the theoretical calculations, the formation constants of Cu(APBO)$_2$ and Cu(APO)$_2$ are 6.93×10^{17} and 5.57×10^{12}, respectively. These are in agreement with the geometries and the difference between HOMO and LUMO calculated energies.
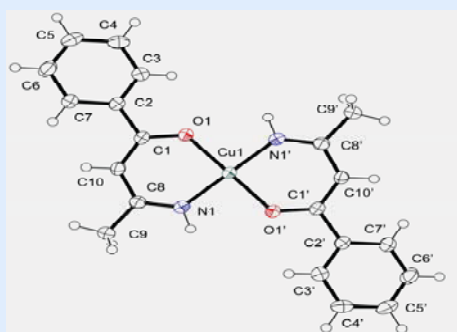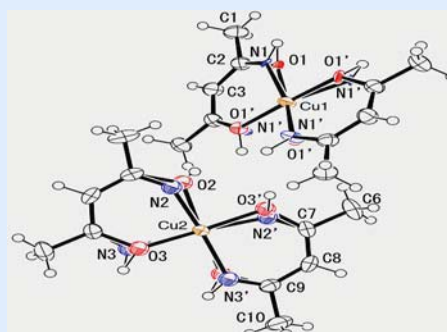

Fig. 1: Cu(APBO)$_2$

Fig. 2: Cu(APO)$_2$

References
[1] Recent reviews: (a) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428-447; (b) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169-1204; (c) S. Mecking, Coord, Chem. Rev. 203 (2000) 325-351; (d) S. Mecking, Angew. Chem. Int. Ed. 40 (2001) 534-540; (e) V.C. Gibson, S.K. Spitzmesser. Chem. Rev. 103 (2003) 283-315.
[2] B.Y. Lee, G.C. Bazan, J. Vela, Z.J.A. Komon, X. Bu, J. Am. Chem. Soc. 123 (2001) 5352-5353.
[3] F.A. Hicks, M. Brookhart, Organometallics 20 (2001) 3217-3219.
[4] F. Bao, R. Ma, Y. Jiao, Appl. Organometal. Chem. 20 (2006) 368-374.
[5] G.E. Gurr, Inorg. Chem. 3 (1964) 614-615.
[6] M. Jamialahmadi, S.F. Tayyari, M.H. Habibi, M. Yazdanbakhsh, S. Kadkhodaei , R.E. Sammelson, J. mol. Struct. 985 (2011) 139-174.

Study on Some Fluorophores For the Explosives Detection Based on Fluorescence Quenching

Ali Reza Zarei, Hadi Motamed Shariati, Behnam Ghazanchayi*

Faculty of Chemistry and Chemical Engineering, Malek Ashtar University of Technology,Tehran, Iran
E-mail address: Behnam.chemistry13@gmail.com.

The analysis of explosives is of great importance in a variety of fields. For example, in landmine detection, in environmental chemistry and in industrial quality control [1]. Because the requirements in each of these fields are so diverse, a versatile method is needed for the analysis of explosives [2]. Previous studies have indicated that explosives may be detected by fluorescence quenching of fluorescent compounds. In the present study, five fluorophores include pyrene, phenol red, malachite green, methylene blue and fluorescein were selected for quenching detection of five explosive compounds which including nitrobenzene (NB) ,4-nitrotoluene (4-NT) ,2,4,6-trinitrotoluene (TNT),2,4-Dinitrotoluene (DNT) and 2,4,6-trinitrotbenzene (TNB). The fluorophores have conjugated, electron-rich structures with significant electron-donating capabilities to facilitate ion-pair formation during the quenching process [3]. The Stern–Volmer constants (K$_d$) were measured for each fluorophore with five explosive compounds. So what happened with quenching fluorescence is an electron transfer complex formation between fluorophores and nitroaromatic explosives compounds. The order of Stern-Volmer constants (K$_d$) observed in all the studied fluorophores were as follows: TNB > TNT > 2,4-DNT > 4-NT > NB. This compounds containing nitro and methyl functional groups attached to the aromatic benzene ring, and the results can be explained by examining the type and number of functional groups cited.. Also, based on the Stern-Volmer constants obtained for fluorophores with nitroaromatic explosive compounds mentioned above were as follows: Pyrene > phenol red > malachite green > methylene blue > fluorescein. The magnitude of the Stern–Volmer constant is representative of the sensitivity of the quenching interaction. For example, Stern–Volmer constants are measured for each fluorophore with TNT equal to 33386, 14086, 4413, 2214 and 1757 (M^{-1}) for pyrene, phenol red, malachite green, methylene blue and fluorescein, respectively. The goal of the present study is to evaluate the selected fluorophores with regard to their potential utility for on-site explosives detection. Promising fluorophores identified from this study may be useful in a variety of field-ready devices, including sensors, wipes, air and water sampling tubes.

Keyword: Fluorescence Quenching, Explosives Detection, Fluorophore, Sensor.

References
[1] S. Casamento, B. Kwok, C. Roux, M. Dawson, P. Doble, J. Forensic Sci. 48 (2003) 1075-1083.
[2] S.R. Wallenborg, C.G. Bailey, Anal. Chem. 72 (2000) 1872–1878.
[3] J.V. Goodpaster, V.L. McGuffin, Anal. Chem. 73 (2001) 2004-2011.