Mechanistic studies on the in-situ generation of furoxan ring during the formation of Cu(II) coordination compound from dioxime ligand : theoretical and experimental study.

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Streszczenie

The copper(II) coordination compound, $[Cu(L')(NO_3)_2]$ (**1**) where **L′** = 3,4-di(pyridin-2-yl)-1,2,5-oxadiazole 2-oxide, was synthesized from the reaction of $Cu(NO_3)_2{\cdot}3H_2O$ and dioxime ligand, (*1E,2E*)-1,2-di(pyridin-2-yl)ethane-1,2-dione dioxime (**L**), in methanol under aerial atmosphere. The dark-blue crystals of **1** were obtained by solvent evaporating method and were characterized by elemental analysis, FT-IR spectroscopy and single crystal X-ray studies. Structural studies indicated that in **1** a furoxan ring is generated during the formation of mononuclear Cu(II) coordination compound from the *in-situ* intramolecular cyclization reaction of dioxime moiety of the initial ligand. The density functional theory (DFT) along with B3LYP functional was employed to propose a rational mechanism for cyclization of dioxime (**L**) and formation of the furoxan ring in **1**. It was found that the isolated ligand (**L**) is not an acidic compound while its acidity is enhanced dramatically in coordination compound in the presence of NO_3^- anions assisting its deprotonation. Ring formation is catalyzed by Cu in the second deprotonation step, i.e. Cu(II) accepts the negative charge of **L**, produced upon deprotonation, to assist formation of the neutral aromatic furoxan ring. In the last step, Cu(I) is oxidized to Cu(II) by solvated oxygen, $O_2(CH_3OH)_n$, to retrieves its structure and oxidation state.

Słowa kluczowe

furoxan, Cu(II) coordination compound, crystal structure, ring formation, mechanism

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