Crystallographic and Computational Electron Density of d_{x2-y2} Orbitals of Azo-Schiff Base Metal Complexes Using Conventional Programs

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In recent years, quantum crystallography, which combines X-ray crystal structure analysis and quantum chemistry, has attracted attention. Attempts have been made to reproduce wave function from electron density obtained from experiments and to refine the crystal structure using computational chemistry [1,2]. However, these attempts require a high degree of expertise and such programs are not widely used. The purpose of this study is to discuss electronic states of azo-Schiff base metal complexes based on quantum chemical calculations and to verify whether quantum crystallography can be performed easily by using conventional programs.

The samples investigated were two Schiff base metal complexes having azobenzene moiety (new **Cu** of *trans*-[CuN_2O_2] and known **Mn** of *cis*-[$CuN_2O_2X_2$]) (Fig. 1) studied on photochemical behavior [3]. Experimental electron density was drawn using a PLATON program. DFT calculation was carried out with a Gaussian09, and electron density analysis and bond order analysis were also performed. Additionally, a CRYSTAL EXPLORER program was used for Hirschfeld surface analysis. Experimental and calculated electron density maps exhibited good agreement (Fig. 2) and gave additional information such as bond strength only with the aid of DFT.

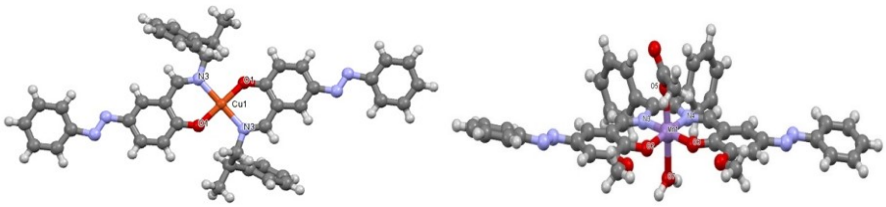

Figure 1. Molecular structures of **Cu** (left) and **Mn** (right)

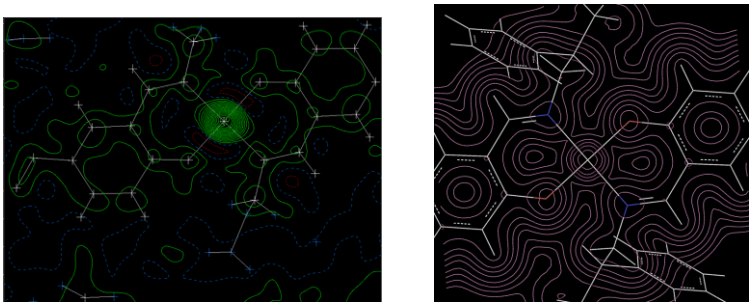

Figure 2. Comparison of experimental (left) and calculated (right) electron densities of **Cu**.

[1] Grabowsky, S.; Genoni, A.; Burgide, H.-B. *Chem. Sci.*, **2017**, *8*, 4159–4176.

[2] Genoni, A.; Bučinský, L. Claiser, N.; Contreras-García, J.; Dittrich, B.; Dominiak, P. M.; Espinosa, E.; Gatti, C.; Giannozzi, P.; Gillet, J.-M.; Jayatilaka, D.; Macchi, P.; Madsen, A. Ø.; Massa, L.; Matta, C. F.; Merz Jr., K. M.; Nakashima, P. N. H.; Ott, H.; Ryde, U.; Schwarz, K.; Sierka, M.; Grabowsky, S. *Chem. Eur. J.,* **2018**, *24*, 10881-10905.

[3] Takiguchi, Y.; Onami, Y.; Haraguchi, T.; Akitsu, T. *Molecules*, **2021**, *26*, 551 (12 pages).

Keywords: Schiff base; metal complex; electron density; coordination bond; DFT

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