Experimental and theoretical charge density study of two tetranuclear transition metal clusters with single molecule magnet properties

Sofie Stampe Leiszner[1], Emil Damgaard-Møller[1], Lennard Krause[1], Khetpakorn Chakarawet[2], Jeffrey R. Long[3] and Jacob Overgaard[1]

[1]Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark. [2]Department of Chemistry, University California, Berkeley, Berkeley, California 94720, United States. [3]Department of Chemistry and Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California 94720, United States; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

jacobo@chem.au.dk

In recent years, Single Molecule Magnets (SMMs) have gained significant attention, primarily due to their potential technological applications in the field of information storage and processing. SMMs are molecules that behaves as small nanomagnets and represents the smallest possible bit that can be used to store binary information. A common method to increase the total spin of such molecule is by engaging several metal centers in a strong ferromagnetic coupling. This strategy is applied in a recent study [1] of the tetranuclear transition metal compounds with formulas $M_4(NP^tBu_3)_4$ (M = Ni, Cu), and the oxidised forms, $[M_4(NP^tBu_3)_4]^+$. These results suggest a strongly coupled, large-spin ground state in the two nickel compounds.

The two non-oxidised compounds, $Ni_4(NP^tBu_3)_4$ and $Cu_4(NP^tBu_3)_4$, are studied here with respect to the bonding interactions between the metal centers. X-ray diffraction experiments have been performed on crystals of both compounds at the synchrotron facility SPring-8 in Japan. Based on the data from the experiments, a multipole model of the charge density is achieved for both complexes. Theoretical structure factors are also calculated based on the experimental atomic positions of the complex containing nickel, and a theoretical multipole model is also developed.

A topological analysis is performed on all three datasets. The plots of the critical points in the charge density show no bond critical points between the metal centers as shown on Fig. 1. This indicates that no bonding is present between the metal centers, which is supported by the results from deformation density plots such as the one in Fig. 2. Plots of the critical points in the Laplacian for the nickel containing complex show that the charge density around the nickel atoms are affected by one another but not strongly, which is supported by calculations of the delocalization index.

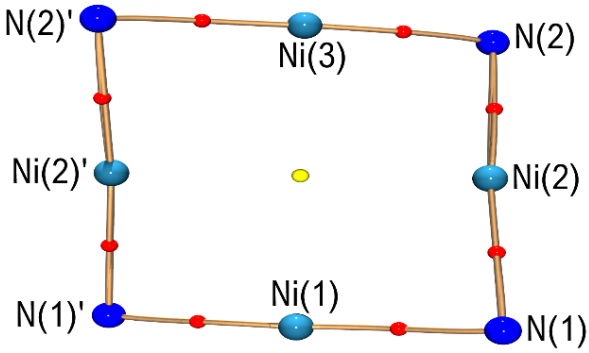

Figure 1: Molecular graph of the central part of the complex containing nickel. Red spheres are bond critical points and the yellow sphere is a ring critical point. Bond paths are marked with golden cylinders.

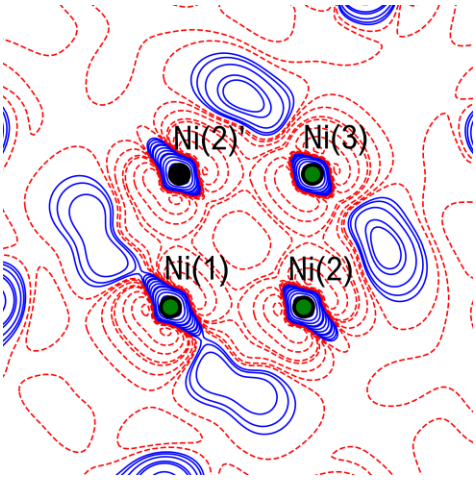

Figure 2: Experimental deformation density in the Ni_4-plane. Dashed red lines indicate negative contours and blue solid lines indicate positive contours.

[1] Chakarawet, K.; Atanasov, M.; Marbey, J.; Bunting, P. C.; Neese, F.; Hill, S.; Long, J. R., Strong Electronic and Magnetic Coupling in M_4 (M = Ni, Cu) Clusters via Direct Orbital Interactions between Low-Coordinate Metal Centers. Journal of the American Chemical Society **2020**, 142 (45), 19161-19169.

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