We have investigated the magnetic and electronic structures of crystalline dimethylammonium copper formate \([\text{(CH}_3\text{)}_2\text{NH}_2\text{Cu(HCOO)}]_3\); a model compound that belongs to a wide class of hybrid organic-inorganic perovskites. We present the results of a combined experimental approach, where neutron diffraction and magnetisation measurements were used to solve the ground state magnetic structure in which the same ligand mediate antiferromagnetic and ferromagnetic interactions, while electron charge density distribution and orbital occupancy were determined by high-resolution x-ray diffraction [1]. The latter provided a microscopic analysis of the chemical bonding from which we established a detailed correlation between the structural, electronic, and magnetic properties of \([\text{(CH}_3\text{)}_2\text{NH}_2\text{Cu(HCOO)}]_3\), demonstrating the primary role of Cu-O bonding in establishing the nature of the exchange (Figure 1). Our results elucidate the mechanism of magnetic exchange mediated by formate anions, from which we examine the applicability of foundational theories of purely inorganic perovskites and define characteristics that the ligands should meet to support the use of the Goodenough-Kanamori-Anderson (GKA) rules [2]. The derived criteria for the applicability of GKA rules where used to predict the magnetic structure, then verified experimentally, of hybrid perovskites including different ligands, such as \([\text{(CH}_3\text{)}_2\text{NH}_2\text{Cu(HCOO)}]_2(\text{NO}_3)\) and \(\text{Cu(HCOO)}_2(\text{pyrimidine})\). Charge density analysis enabled us to account for qualitative and quantitative differences in the superexchange mediated by formate, nitrate and pyrimidine.

**Figure 1.** Spatial electronic configuration of Cu\(^{2+}\) ions pertinent to superexchange via molecular (formate) ligands, as determined by quantum crystallography in \([\text{(CH}_3\text{)}_2\text{NH}_2\text{Cu(HCOO)}]_3\). Blue and red contours (0.2 e/Å\(^3\)) for excess and depletion of electron density. Yellow sticks depict Jahn-Teller elongated bonds. Inset: schematic representation of GKA rules.

[1] R. Scatena, R. D. Johnson, P. Manuel, P. Macchi, *J. Mater. Chem. C* 2020, 8, 12840–12847.

[2] S. V. Streltsov, D. I. Khomskii, *Uspekhi Fiz. Nauk* 2017, 187, 1205–1235.