The electronic structure of molecular Pt clusters from solid-state ^{195}Pt NMR, one atom at the time.

D. Gioffrè[1], A. Yakimov[1], C. Copéret[1]*

[1]Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland

Atomically-precise metal clusters show unique properties which make them appealing for the preparation of optical devices and for biomedical applications. Furthermore, some of these species are proposed to be catalytically active for the activation of small molecules and for selective transformations of organics. As such, they provide fundamental knowledge on the bonding and reactivity of complex systems.[1]

Common characterization techniques of metal clusters involve mass spectrometry, optical and X-ray spectroscopies.[2,3] While these tools can describe a system in its totality, they only provide an averaged information of the different metal sites. Conversely, solid-state NMR (ss-NMR) spectra encode information on the electronic structure of a specific nucleus, as the shape and orientation of the chemical shift (shielding) tensor (CST) is strictly related to its valence orbitals (fMOs).[4]

In this work, we show how ^{195}Pt ss-NMR can be used to understand the bonding situation of metal nuclei in a library of $Pt_n(0)$ species with different nuclearity (n= 1 to 5) and connectivity.[5] ss-NMR can be therefore applied as a general tool to distinguish among the metal sites of clusters. Additionally, the analysis of the CST of a nucleus in a cluster can provide information on its local electronics and environment (**Figure 1**).

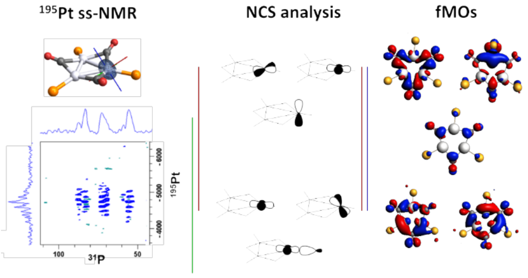

Figure 1: Investigation of a $Pt_3(CO)_3(PR_3)_3$ cluster: $^{31}P\{^{195}Pt\}$ ss-NMR, CST and MOs responsible for the (de)shielding.

[1] Chakraborty, I.; Pradeep, *T. Chem. Rev.*, **2017**, 117, 8208-8271.
[2] Joshi, C. P.; et.al, *J. Am. Chem. Soc.*, **2015**, 137, 11578-11581.
[3] Zhang, B.; et. al., *ChemCatChem*, **2018**, 10, 5372-5376.
[4] Venkatesh, A.; Gioffrè, et. al., *J. Am. Chem. Soc.*, **2022**, 144, 13511-13525.
[5] Chatt, J.; Chini, *P., J. Chem. Soc. Inorg. Phys. Theor.*, **1970**, 0, 1538-1542.