Kondo effect in binuclear metal-organic molecules on metallic surfaces

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Recent low temperature STM measurements performed by Wulf Wulfhekel's group (Physikalisches Institut, KIT) on a binuclear metal-organic molecule, (Ni(hexafluoro-acetylacetonate)$_2$)$_2$bipyrimidine [(Ni(hfacac)$_2$)$_2$(bpym),"Ni$_2$"], deposited on a Cu surface reveal that the system undergoes a Kondo effect with a spin located nearby Ni atoms and Kondo temperature T_K of the order of ~10K, which is adsorption-type dependent. The physics in play is intriguing, because the synthesized molecule does not have anchoring groups, which could be responsible for a formation of a chemical bond with the Cu surface. Without such bonds the relatively high T_K is difficult to rationalize.

In this contribution, we will report a theoretical work aiming to shed light onto the puzzle. By comparing experimental data with simulated STM images computed via our embedded density functional theory (DFT) approach [J. Wilhelm *et al.*, PCCP **15**, 6684 (2013); A. Bagrets, J. Chem. Theo. Comp. **9**, 2801 (2013)] we have identified possible adsorption geometries. Van der Waals bonding is not compatible with large Kondo temperatures observed experimentally and thus is discouraged. Our simulations show that some STM images could be attributed to a distorted "Ni$_2$" complex with partially weakened internal chemical bonds (figure below), while other STM images may be interpreted as arising from molecular fragmentation. We propose that in experiments a Ni(hfacac)$_2$ moiety is seen, which establishes a bond to the Cu surface via a Ni atom.

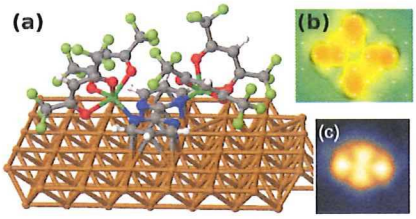

Figure: (a) possible arrangement of the "Ni$_2$" binuclear complex on a Cu(001) surface; (b) simulated constant current STM image and (c) experimentally recorded low temperature STM image of the molecule.

In the latter case our investigations of the local Kohn-Sham spectral function at Ni atom show that the Kondo effect arises mainly due to unpaired electron populating a d_{z2} type orbital, where a line width (Γ) of the molecular resonance is sensitive to the binding strength of the molecule to a substrate. Since Γ also enters the Kondo temperature T_K, DFT can predict a trend for the dependency of T_K on the strength of the coupling of the molecule to a metallic surface that can be confronted against experimental data. In the case of "Ni$_2$" complex (figure above), our analysis provides evidence that the Kondo effect originates from a pair of weakly coupled S=1 spins, where low energy spin excitations are likely seen in the experimental data.