Kondo effect in binuclear metal-organic complexes with weakly interacting spins

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We report a combined experimental and theoretical study of the Kondo effect in a series of binuclear metal-organic complexes \([(\text{Me(hfacac)}_2)_2(\text{bpym})]_0\), referred to later on as “Me2” (see Fig. 1). These complexes have been deposited on a clean Cu(001) surface and studied with low-temperature scanning tunneling microscopy (STM). While no feature of the Kondo effect was found in the scanning tunneling spectroscopy (STS) spectrum of Zn2 with closed-shell 3d ions, an adsorption-site dependent zero-bias (Kondo) resonance was clearly resolved in the case of Mn2 and Ni2 complexes (see Fig. 2).

The Ni2 case is particularly interesting, as the adsorbed molecule appears in two variants that differ in STM images and STS characteristics. To rationalize these observations, we have performed calculations based on density functional theory (DFT). We thus identify possible adsorption geometries. Our simulations show that one observed geometry (with relatively large Kondo temperature \(T_K \approx 10 \text{K}\)) can be attributed to distorted Ni2 complexes, which are chemically bound to the surface via the bipyrimidine unit. The other geometry we assign to molecular fragmentation: we suggest that the original binuclear molecule decomposes into two pieces, including Ni(hexafluoroacetylacetonate)2, when brought into contact with the Cu substrate. For both geometries our calculations support a picture of the \((S = 1)\)-type Kondo effect emerging due to open 3d shells of the individual Ni2+ ions.

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I. INTRODUCTION

Molecular electronics holds the vision that functional electronic devices, like memory elements, rectifiers, and transistors, may be realized by designing suitable molecular complexes. Over the past decade, two- and three-terminal molecular junctions with current-voltage characteristics resembling diod- [1,2], transistor- [3–5], or memorylike [6,7] behavior have been demonstrated. The function of molecular devices can be achieved using the spin degree of freedom initiating the field of molecular spintronics. An important step in this direction was made recently, when a giant magnetoresistance effect has been demonstrated for single molecule magnets (SMMs) [25]. Interesting active spin, say two exchange coupled spins that anticipate the Kondo effect, such as Kondo screening, and the intermolecular exchange coupling.

Motivated by such a question, we have synthesized a series of binuclear metal-organic complexes of the form \([(\text{Me(hfacac)}_2)_2(\text{bpym})]_0\), referred to later on as “Me2” (see Fig. 1). These complexes have been deposited on a clean Cu(001) surface and studied with low-temperature scanning tunneling microscopy (STM). While no feature of the Kondo effect was found in the scanning tunneling spectroscopy (STS) spectrum of Zn2 with closed-shell 3d ions, an adsorption-site dependent zero-bias (Kondo) resonance was clearly resolved in the case of Mn2 and Ni2 complexes (see Fig. 2).

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II. SYNTHESIS AND CHARACTERIZATION OF BINUCLEAR COMPLEXES

Molecular geometries. The molecular structure of the neutral binuclear metal complexes \([(\text{Me(hfacac)}_2)_2(\text{bpym})]_0\), with Me = nickel (II), manganese (II), zinc (II); hfacac = hexafluoroacetylacetonate, and bpym = bipyrimidine, studied in this work is presented in Fig. 1. The structural details of the metal complexes, in particular the coordination environment of the metal ions, are sensitive to the kind of 3d metal ion involved (for details, see the Supplemental Material [35], Sec. IV). According to single-crystal x-ray diffractionometry [46] each
Mn$^{2+}$ ion is situated in a distorted trigonal prismatic N$_2$O$_4$ coordination sphere leading to a Mn-Mn distance of 6.2 Å in Mn$_2$ dimer. By contrast, the Ni$_2$ complex exhibits a distorted coordination sphere leading to a Mn-Mn distance of 6.2 Å in Mn$_2$.

**Magnetism.** The magnetic behavior of polycrystalline samples of the Mn$_2$ and Ni$_2$ complexes was determined between 2 and 300 K (Supplemental Material [35], Sec. IV). At room temperature Mn$_2$ has a χ$_M$T value of 9.03 cm$^3$Kmol$^{-1}$ (here χ$_M$ is the molar magnetic susceptibility and T is the temperature), corresponding to two uncoupled high-spin Mn(II) ions with a spin value of $S=5/2$ each, while Ni$_2$ shows a χ$_M$T product of 2.23 cm$^3$Kmol$^{-1}$, corresponding to two uncoupled Ni(II) ions with $S=1$. Between 300 and 75 K both the Mn$_2$ and Ni$_2$ complexes show paramagnetic behavior, while below 75 K weak antiferromagnetic (AF) behavior sets in. The AF exchange interaction between the two divalent 3d ions through a bpyrm bridging ligand is reported as $J_{ex}^{AF}$ = 1.6 meV [48] and $J_{ex}^{AF}$ = 2.06 meV [47] for Ni$_2$, which is about ten times larger than the exchange interaction observed in Mn$_2$ with $J_{ex}^{AF}$ = 0.13 meV.

**DFT calculations for the Ni$_2$ complex.** The spin state of each of the two Ni(hfacac)$_2$ units was determined as $S = 1$ assuming an [Ar]3d$^8$ electronic configuration for the Ni$^{2+}$ ion. Specifically, the atomic structure of the nonadsorbed (gas-phase) Ni$_2$ complex was refined starting from the x-ray-diffraction structure with Ni$^{2+}$ ions in distorted octahedral environment (see Supplemental Material [35], Sec. I, for computational details). The results of the “constrained” DFT calculations are summarized in the first row of Table I. In particular, our calculations predict a “singlet” ground state with the two spins, $S = 1$, coupled antiferromagnetically. For the gas-phase complex, very low excitation energy ($\sim$15 meV) is observed with an excited state exhibiting ferromagnetic coupling. Our results are consistent with experimental findings: weak antiferromagnetic exchange interaction between the two metal ions of the [(Me(hfacac)$_2$)$_2$(bpyrm)]$^0$ complexes facilitated by the bpyrm ligand has been reported before [47].

**III. STM EXPERIMENTS**

The STM experiments were performed using a home-built, low-noise STM operating between 0.7 and 4.2 K in ultrahigh vacuum (UHV) ($p < 10^{-9}$ mbar) [51]. Clean and atomically flat Cu(100) substrates were prepared in situ followed by deposition of molecules by sublimation at 80–100°C. Three adsorption configurations, $\alpha$ (Ni$_2$ and Zn$_2$), $\beta$ (only Ni$_2$), and $\gamma$ (Mn$_2$ and Ni$_2$), of the molecules on Cu(100) were found [see Figs. 2(a)–2(e)]. Scanning tunneling spectroscopy (STS) measurements were performed on these different configurations. Kondo-like peaks were clearly resolved in the $dI/dU$ curves of Mn$_2$ and Ni$_2$ (in both configurations) near the Fermi level while no remarkable feature was found in the $dI/dU$ curve of the nonmagnetic Zn$_2$ complexes [see spectra displayed in Fig. 2(f)].

The Kondo effect arises when the magnetic moment of an impurity is screened by surrounding electrons of a nonmagnetic substrate [52,53]. As the simplest manifestation of the interaction between the localized spin and delocalized electrons, the shape of the zero-bias anomaly in STS caused by the Kondo effect can be described by a Fano resonance [54–56]:

$$\frac{dI}{dU}(U) \propto \frac{(\varepsilon + q)^2}{1 + \varepsilon^2},$$

where

$$\varepsilon = \frac{eU - \varepsilon_0}{\Gamma},$$

$$\Gamma = 2 \varepsilon_0.$$
and \( \varepsilon_0 \) is the energy shift of the resonance from the Fermi level, \( \Gamma \) is the width of the resonance. The Fano parameter \( q \) characterizes the interference of tunneling between the tip and the magnetic impurity and tunneling between the tip and the sample \[57\]. Considering the temperature dependence, the Kondo resonance can be approximated by a Lorentzian resonance \[58\]. Thus the energy width \( 2\Gamma(T) \) (full width at half maximum) of a Kondo resonance can be expressed as

\[
2\Gamma(T) = 2\sqrt{\left(\frac{\pi k_B T}{2}\right)^2 + (k_B T K)^2},
\]

(3)

with \( k_B \) being the Boltzmann constant, \( T \) being the environment temperature, and \( T_K \) being the Kondo temperature. By fitting the experimental STS with Eqs. (1)–(3), the Kondo temperature \( T_K \) is extracted.

The Zn\(^{2+}\) ions in the complex are expected to have a full 3\(d\) subshell, so a magnetic moment is absent. This is in agreement with the superconducting quantum interference device measurements of the crystals of this complex. Thus, a Kondo effect could appear only in adsorbed molecules if a charge transfer between the molecule and the substrate leads to the acquisition of a magnetic moment on the molecule. Since our measurements do not indicate a Kondo resonance [compare Fig. 2(f)], we conclude that the interaction with the substrate is too weak for such a charge transfer. Contrary to Zn\(^{2+}\), in Mn\(_2\) and Ni\(_2\) the central Mn\(^{2+}\)/Ni\(^{2+}\) ions exhibit a partially filled 3\(d\) shell and therefore carry a finite magnetic moment. They are at the origin of the Kondo effect that we observe in our measurements, Fig. 2. By fitting to the Fano-shaped resonance, a Kondo temperature of 15 K for Mn\(_2\) is determined.

With Ni\(_2\) the situation is more complex since two different adsorption geometries (referred to as \( \alpha \) and \( \beta \)) are observed; see Figs. 2(b) and 2(c). We determine two Kondo temperatures, 5.8 and 16 K for Ni\(_2\)-\(\alpha\) and Ni\(_2\)-\(\beta\), respectively. An even clearer difference between these adsorption geometries exhibits itself in a site-dependent STS measurement that we perform on Ni\(_2\)-\(\alpha\) and Ni\(_2\)-\(\beta\); see Fig. 3. The measurement shows that the Kondo resonance has a single maximal amplitude at the center of the Ni\(_2\)-\(\alpha\) complex [cf. Figs. 3(a) and 3(e)], while two spots with maximal amplitude of \( dI/dU \) signal separated by a distance of 4 \( \AA \) are clearly resolved in the STS map of Ni\(_2\)-\(\beta\) [cf. Figs. 3(b) and 3(d)], which match the two Ni\(^{2+}\) ions and their expected distance in the molecule.

At first sight, these results suggest that adsorption configurations of Ni\(_2\) complexes may look like those shown in Figs. 3(e) and 3(f). Namely, Ni\(_2\)-\(\beta\) could correspond to the molecular complex, which “lies” on the surface with both of its hfcc ligands, thus exposing the two Ni ions separately to the STM tip. The \(\alpha\) configuration could correspond to the complex, which “stands” on the surface with one hfcc ligand and the other hfcc ligand is seen in its topographic image. This would expose the two Ni ions above each other such that a single Kondo resonance is observed in STS. As we show later on, the latter assignment is inconsistent with the theoretical considerations. Below, we propose an alternative scenario.

### IV. THEORY

To elucidate microscopic details of the Kondo-effect observed experimentally, we have performed elaborate DFT calculations. Our main objective is to understand the dependence of the Kondo resonance of the Ni\(_2\) complex on the adsorption site. Additional questions that we address will concern the nature of molecular orbitals involved in the interaction with conduction electrons, and how delocalized electrons compete for screening of the initially antiferromagnetically coupled spins.

#### A. Simple adsorption geometries

We analyze the adsorption geometries schematically illustrated in Figs. 3(e) and 3(f). They exhibit gas-phase Ni\(_2\) complexes placed on Cu(001) surface (see Supplemental Material \[35\], Sec. II A, for computational details). Our simulation results indicate fluorine-copper distances above \( \sim 3 \) \( \AA \). This distance implies that a weak van der Waals (vdW) force dominates binding to the surface. There is only a weak hybridization between molecular and substrate states, which translates into narrow molecular resonances, \( \Gamma \approx 10 \) meV, as seen from the spectral function \( A(E) \) projected on the Ni(II) ion (see Supplemental Material \[35\], Suppl. Fig. 2). Giving typical parameters of the Anderson model \[59\] read from \( A(E) \), namely, single occupied resonance level width \( \Gamma \approx 10^{-2} \) eV, on-site Coulomb repulsion energy \( U \sim 2 \) eV, and position of the resonance level \( \varepsilon_d \sim U/2 \sim 1 \) eV relative
to the Fermi energy, we can estimate the Kondo temperature as \[ k_B T_K \sim U \frac{1}{\pi} \exp(-\pi U/4) \sim 0.1 \times 10^{-6} \, \text{eV} \sim 10^{-69} \, \text{eV}. \] This result contradicts the experimental finding of \( k_B T_K \sim 10 \, \text{meV} \), so that we exclude adsorption geometries shown in Figs. 3(e) and 3(f). An intuitive assumption for the adsorption configurations of Ni\(_{2-}\alpha\) and Ni\(_{2-}\beta\) (front view) on the Cu(100) substrate is shown in (c) and (d), respectively.

**B. \( \alpha \) configuration: Ni(hfacac)\(_2\) fragments on Cu(001)**

In order to enforce a much larger coupling of the molecular complex to the substrate we first consider the extreme case of molecular fragmentation; see Fig. 4(a). Here we include the possibility that coordination bonds between the Ni\(_2^+\) ion and nitrogen atoms are broken, and a Ni(hfacac)\(_2\) moiety, which is chemically bound to a Cu surface, is observed in the experiment. In that situation the coupling of the spin to the Cu surface is comparable to the case of a single Ni adatom (no ligands attached), and drawing from related earlier experimental experience [16,17,66] one might suspect Kondo temperatures of the order of tenth of meV roughly consistent with the present measurements. In order to show that the fragmentation scenario is consistent with the experimental findings, we observe the following facts:

(i) Simulated STM-images. Our simulations of fragmented molecules [Figs. 4(d) and 4(e)] yield STM images reproducing the most important characteristics of the experimental ones for Ni\(_{2-}\alpha\): the outermost contours have a butterfly shape, two mirror planes exist, the size of experimental and computational images are consistent. It is encouraging to see that also nontrivial details are (partially) reproduced. Namely, theory predicts a nonzero optimal angle, \( 45^\circ \) [Fig. 4(b)] that fixes orientation of the fragment’s mirror planes vs the fcc [100] direction of the (001) surface plane (see also Supplemental Material [35]). In contrast, the experimentally observed angle, \( \approx 25^\circ \), is also observed in the representative experimental images of Ni\(_{2-}\alpha\) (see Suppl. Fig. 5).

(ii) Spatial dependency of Kondo amplitude. The fragment’s geometry is such that the associated Kondo resonance would have maximum amplitude with the STM tip located in the center of the image (at the Ni atom). That is consistent with the structure of the spatially resolved Kondo resonance of Ni\(_{2-}\alpha\) observed experimentally [cf. Figs. 2(a) and 2(c)].
ligands, that the s electrons are effectively transferred to ligand orbitals. Therefore, the metal ion takes the Ni$^{2+}$ configuration and exhibits two unpaired spins. We performed a DFT study within the generalized gradient approximation (GGA). Perdew-Burke-Ernzerhof exchange-correlation functional [67]) of the molecule in gas phase (for details, see Supplemental Material [35], Sec. I). Our results confirm the above picture: we find a spin-polarized ground state with a magnetic moment of 2$\mu_B$. The magnetization is largely due to two orbitals ($a$ and $b$ in Fig. 5) that are populated with up-spin electrons, only, and that contribute substantial weight to both Ni $d_{z^2}$ and $d_{xy}$ atomic states.

One may ask whether the fragment keeps its magnetic moment when adsorbed on the substrate. To answer this question, we performed another spin-DFT study, whose details are presented in the Supplemental Material [35] (Sec. II and Suppl. Fig. 3). In essence, the substrate further breaks the residual degeneracy of the $d$ orbitals splitting $d_{z^2}$ and $d_{xy}$ by 1.4 eV. As a result, $d_{z^2}$ is nearly full (0.4 eV below $E_F$), while $d_{xy}$ is nearly empty (1 eV above $E_F$ with resonance $\Gamma_b \approx 10^{-2}$ eV). The magnetization drops after adsorption by about a factor of 2, down to 1.2$\mu_B$. The net charge-electron transfer to the molecule in the adsorption process is 0.4e.

The GGA-type calculation leaves us with a situation where a localized $3d_{z^2}$-type orbital is only partially occupied. In DFT with conventional local exchange-correlation (XC) functionals (local-density approximation, GGA) this is typically an indication of correlation physics, such as the Coulomb blockade. The Coulomb blockade is not described by conventional DFT functionals, but it can be captured on the level of GGA+$U$ [68,69]. Therefore, following Ref. [70], we performed a GGA+$U$ calculation placing a repulsive on-site term with (relatively large) strength $U = 6$ eV on the metal site. (Details of our implementation are given in Ref. [71].) The interaction shifts the spin-down resonance $a$ from 0.4 eV below to 0.5 eV above $E_F$ (Fig. 5). Hence, the magnetic moment increases up to 1.62$\mu_B$ thus suggesting the picture of the ($S = 1$) Kondo effect.

So far our $ab$ initio study has ignored the spatial structure of the two molecular orbitals involved, orbital $a$ with substantial contribution from Ni $d_{z^2}$ atomic state, and orbital $b$ with substantial contribution from Ni $d_{xy}$ atomic state. These molecular orbitals are depicted in Fig. 5. As can be seen, the $a$ orbital (first quantum dot, $\Gamma^*_a$) is directed towards the surface. Hence, it hybridizes with the substrate much stronger than the $b$ orbital (second dot $\Gamma_b$), i.e., $\Gamma^*_b \ll \Gamma^*_a$. Each level has a single occupancy and the electrons populating them are coupled ferromagnetically. Since the exchange interaction (∼0.5 eV, see Table I) is much larger compared to the expected Kondo energy scale ∼10 K, both spins form a triplet, $S = 1$. Reading parameters from the spectral function (Fig. 5),

$$\Gamma_a \simeq 0.8 \text{ eV} \gg \Gamma_b; \quad \epsilon_d \simeq 0.5 \text{ eV}; \quad U \simeq 5.5 \text{ eV} \gg \epsilon_d,$$

and using a formula [60,61] for the Kondo temperature,

$$k_B T_K \simeq 0.41 U \left( \frac{\Gamma^*}{4U} \right) e^{-\pi \epsilon_d / \Gamma^*},$$

where $U \gg \epsilon_d$ and $\Gamma^* = \Gamma_a/2$ for the case of the double-dot system, we obtain $k_B T_K \simeq 5.84 \times 10^{-3}$ eV, i.e., a

![Ni(hfacac)$_2$ moiety on Cu (001)

GGA (PBE) + $U$ (= 6 eV)

Local density of states at Ni atom ($1/eV$)

KS energy, $E - E_F$ (eV)

Ni atom $d_{z^2}$ states
$d_{xy}$ states

(a) $\alpha$
(b) $\beta$

FIG. 5. (Color online) Upper plot: spin dependent local density of states projected on Ni atom of the Ni(hfacac)$_2$ on Cu(001). Red and blue lines highlight contributions to the LDOS associated with Ni $d_{z^2}$ and $d_{xy}$ orbitals. Lower plots: corresponding Kohn-Sham wave functions of the free standing molecule.
Kondo-temperature $\approx 70$ K in qualitative agreement with the experiment. We emphasize that a more precise estimation of the Kondo temperature is hampered by exponential dependence of $T_K$ on model parameters. For example, taking into account that DFT has a tendency to overestimate resonance linewidths, we may assume a slightly smaller $\Gamma_a \approx 0.6$ eV. This reduces $T_K$ down to $\approx 16$ K, which is in good agreement with the experimentally observed value.

**C. $\beta$ configuration: Distorted Ni$_2$ complex on Cu(001)**

Spatially resolved intensity of the Kondo resonance, measured on top of the Ni$_2$-$\beta$ image [Fig. 3(d)] suggests that also molecular species with two metal ions are to be found on a Cu surface. To rationalize this observation, we performed numerical simulations, to find an intact but strongly distorted molecular conformation [see Fig. 6(g)] that establishes a chemical bond to the Cu surface—an important prerequisite for observable Kondo temperatures. This bond is presumably realized via the delocalized $\pi$ orbitals of the central bpym unit overlapping with the electron density extending from the surface. The bond involves contributions of the vdW forces [62], which have been accounted for in our simulations, and presumably has ionic character due to fractional charge transfer to the quasidegenerate lowest unoccupied molecular orbitals (LUMOs) [72].

We mention that even for the modern ab initio methods, finding the relaxed ground-state structure of a large organic molecule (such as Ni$_2$ complex) on a surface is a nontrivial procedure. Due to the many atomic degrees of freedom involved, relaxation can end up in different molecular conformations with energies differing by $\sim 100$ meV, as was also the case in our simulations. To be specific in the following discussion, we focus on two representative but slightly different conformations of “distorted” Ni$_2$ complex (for details, see Suppl. Fig. 4).

The first conformation [see Suppl. Fig. 4(a)] has been obtained within the preliminary DFT relaxation procedure: the atomic structure of the complex has an (approximate) $C_{2v}$ symmetry, in registry with the underlying fcc(001) surface. For this conformation, the simulated STM image of the complex reveals a “crosslike” structure, resembling Ni$_2$-$\beta$ experimental images [see Figs. 6(a), 6(c), and 6(e)]. Further relaxation steps within the simulation account for an energy gain of about $\sim 0.25$ eV: the local symmetry of the molecular complex is broken resulting in the second conformation [see Suppl. Fig. 4(b)]. Then formerly symmetric simulated crosslike STM images are transformed to the ones with broken symmetry [cf. Figs. 6(d) and 6(f)], which were also experimentally observed [cf. Fig. 6(b)].

The structure of the binuclear complex suggests that the molecular spins should reside on the Ni(hfacac)$_2$ units, where each unit could accept two unpaired electrons (referred to as $S = 1$) owing to $[\text{Ar}]3d^8$ electronic configuration of the Ni$^{2+}$ ion. Essentially, the two $S = 1$ subsystems are magnetically nearly decoupled, since only a weak indirect (“superexchange”) interaction between them could be realized via the $\pi$ orbitals of the bpym unit. Thus, we anticipate that each subsystem will develop a Kondo effect, independently, as the molecular complex provides two parallel conduction paths (channels) for the tunneling electron, one for each spin.

These expectations are fully confirmed by our computational analysis. Constrained DFT calculations (see data in Table I) predict a “singlet” ground state with antiferromagnetically (AF) coupled $S = 1$ spins. For the distorted Ni$_2$ complex, the state with ferromagnetically (F) coupled $S = 1$ spins is only $\sim 2$ meV above the AF state.

The frontier molecular orbitals (see Fig. 7, bottom panels) carry unpaired spins (ferromagnetic coupling between $S = 1$ subsystems is considered there) confirming the above picture: two out of four orbitals, $a$ and $b$, are primarily localized on the left-hand side of the Ni$_2$ complex, while their counterparts, $a'$ and $b'$, are localized on the right-hand side. When the Ni$_2$ complex is brought in contact with the Cu surface, these molecular orbitals are transformed to resonances ($a,b,a',b'$) in the spectral function centered around $\sim 1.5$ eV below the Fermi level $E_F$ (see Fig. 7), while the upper Hubbard band ($a''$) is placed just above $E_F$. Furthermore, since the wave functions $a$ and $a'$ involve larger contributions from $\pi$ orbitals of the central bpym unit, the corresponding resonances $a$ and $a'$ are much broader than the $b$ and $b'$ ones.

Assuming that the weak AF coupling between the two subsystems is below the Kondo temperature, $J_{AF} = (E_{AF} - E_F)/2 \approx 12$ K $\leq T_K$ (otherwise the AF singlet ground state would

*FIG. 6. (Color online) Experimentally recorded (a), (b) Ni$_2$-$\beta$ and simulated STM images of the Ni$_2$ complex, with partially weakened chemical bonds, bound to Cu(001) via the bpym moiety [see lower plot (g)]. Theoretical images are computed with VASP [63] (c),(d) and AITRANSS [65] (e),(f). Images (c) and (e) are obtained assuming symmetry constraints within the DFT relaxation procedure, while images (d) and (f) correspond to the relaxed structure without constraints (see text for further details). Lower plot (g) shows distorted Ni$_2$ complex with partially weakened chemical bonds bound to Cu(001) via (bpym) moiety.*
FIG. 7. (Color online) Upper plot: spin-dependent local density of states projected on one of the Ni atoms of the distorted Ni2 complex deposited on Cu(001) [for a geometrical arrangement, see Fig. 6(g)]. Middle (zoomed in) plot shows majority (up-) spin spectral function below the Fermi level, where contributions are highlighted arising from four orbitals \((a, b, a', b')\), each carrying one unpaired spin. Corresponding wave functions are presented below. There \(a\) and \(b\) are localized on the left-hand side, while \(a'\) and \(b'\) are localized on the right-hand side of the molecular complex.

be incompatible with the Kondo effect observed experimentally), each subsystem will undergo Kondo screening independently below the Kondo temperature. We note that due to the inversion center, each spin has its own conduction channel [73]. Using Eq. (4) (limit \(U \gg \varepsilon_d\)), and parameters read from the computed spectral function (see Fig. 7),

\[
2\Gamma^* = \Gamma_{a,a'} \simeq 0.1 \text{ eV} \gg \Gamma_{b,b'},
\]

\[
\varepsilon_d \sim 0.06-0.125 \text{ eV}, \quad U \simeq 1.5 \text{ eV} \gg \varepsilon_d,
\]

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D. Satellites accompanying the Kondo resonance

Yet another intriguing experimental observation, found in the differential conductance \(dI/dU\) of Ni2-\(\beta\), are two satellites at \(\pm 30 \text{ mV}\) (Fig. 8). We discuss further four possible hypotheses, which might explain their origin. These are (a) parallel conduction through frontier molecular orbitals (LUMOs); (b) low-energy magnetic excitations from the singlet ground state within the binuclear complex; (c) zero-field splitting of the triplet state of Ni2\(^{2+}\) ion; and (d) low-energy vibrational excitations of the complex and associated with that phonon-assisted Kondo effect. According to the analysis presented below, three hypotheses, (a), (b), and (c), are likely to be ruled out in favor of hypothesis (d).

**Hypothesis (a).** The first plausible suggestion is that satellites in \(dI/dU\) around the Kondo resonance may be attributed to the parallel conduction through the LUMO and LUMO+1 of a Ni2 complex, as summarized in Fig. 9. A distorted gas-phase Ni2 complex has almost degenerate LUMO and LUMO+1 levels (e.g., in the minority spin channel, if Ni spins are coupled ferromagnetically), with splitting \(\Delta \simeq 0.08 \text{ eV} \) comparable with the required energy scale \(2\delta E \simeq 0.06 \text{ eV}\). A pair of LUMO and LUMO+1 wave functions [see Fig. 9(c)] involve \(d\) orbitals of two Ni\(^{2+}\) centers hybridized via \(\pi\) states of the central bpym unit. When the Ni2 complex is deposited on a Cu surface (Fig. 6), molecular orbitals hybridize with the substrate states in different ways [72], as seen from Figs. 9(a) and 9(b). Two “satellites” are seen in the DFT spectral function \(A(E)\): below \(E_F\) (a “shoulder” of the partially occupied LUMO state) and above \(E_F\) (mainly, LUMO+1 resonance) [74]. However, these satellites are placed at energies around \(\pm 100 \text{ meV}\) vs the Fermi level, i.e., above the required energy \(\delta E \simeq 30 \text{ meV}\). Their positions in the spectral function \(A(E)\) are furthermore sensitive to the variations in the absorption geometry [cf. Figs. 9(a) and 9(b)], and it is unlikely that the found satellites are always expected at equidistant points with respect to the Fermi level.

**Hypothesis (b).** Following the data presented in Table I, also magnetic excitations are unlikely to be the cause. A transition from AF to F coupling of \(S = 1\) spins happens at the energy scale \(~ 2 \text{ meV}\), too small to explain peaks at \(\pm 30 \text{ meV}\).
Furthermore, the AF singlet ground state is not compatible with the observed Kondo effect. Furthermore, breaking Hund’s rule and flipping a 1/2 spin at the Ni^{2+} center is too expensive (~0.5 eV; see Table I).

**Hypothesis (c)**, relies on zero-field splitting of a triplet $S = 1$ state (we refer here to one of the magnetically almost isolated subsystem—a Ni(hfacac)$_2$ unit with a single Ni$^{2+}$ center). Because of spin-orbit interaction, the triplet splits into a (quasidegenerate) doublet and a singlet, with the lowest energy state to be dependent on the sign of the largest anisotropy constant $D$ in the zero-field spin Hamiltonian, $H_{ZF} = D[S^2 - S(S + 1)/3] + E(S^2_z - S^2_x)$. An experimental evidence exists, Ref. [75], that for example under a strong distortion of the octahedral symmetry splitting can be of a few meV. However, if $D > 0$, the ground state is singlet, while the doublet is accessible at nonzero bias voltages only corresponding to a split Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D < 0$, the ground state is singlet, and the doublet is accessible at nonzero bias voltages only corresponding to a Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D > 0$, the ground state is singlet, while the doublet is accessible at nonzero bias voltages only corresponding to a split Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D < 0$, the ground state is singlet, and the doublet is accessible at nonzero bias voltages only corresponding to a split Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D > 0$, the ground state is singlet, while the doublet is accessible at nonzero bias voltages only corresponding to a Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D < 0$, the ground state is singlet, and the doublet is accessible at nonzero bias voltages only corresponding to a split Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D > 0$, the ground state is singlet, while the doublet is accessible at nonzero bias voltages only corresponding to a Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D < 0$, the ground state is singlet, and the doublet is accessible at nonzero bias voltages only corresponding to a split Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D > 0$, the ground state is singlet, while the doublet is accessible at nonzero bias voltages only corresponding to a Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D < 0$, the ground state is singlet, and the doublet is accessible at nonzero bias voltages only corresponding to a split Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D > 0$, the ground state is singlet, while the doublet is accessible at nonzero bias voltages only corresponding to a Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D < 0$, the ground state is singlet, and the doublet is accessible at nonzero bias voltages only corresponding to a split Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D > 0$, the ground state is singlet, while the doublet is accessible at nonzero bias voltages only corresponding to a Kondo resonance, a situation that is not observed experimentally. Contrarily, if $D < 0$, the ground state is singlet, and the doublet is accessible at nonzero bias voltages only corresponding to a split Kondo resonance, a situation that is not observed experimentally.

To verify this idea, we have performed quantum-chemistry calculations of the electron-phonon coupling matrix elements for the Ni$_2$ complex. To simplify our analysis, we have considered a distorted molecular conformation of Ni$_2$ with imposed $C_{2v}$ symmetry that closely resembles the atomic structure of the complex preoptimized nearby a Cu(001) surface [see Suppl. Figs. 1(b) and 4(a) in the Supplemental Material [35]].

To first order, molecular vibrations of two Ni(hfacac)$_2$ units can be considered independently, since these units are attached to the bpm moiety, which is strongly bound to the Cu surface. Therefore, we consider one of the Ni(hfacac)$_2$ units and define an “active” subspace limited to 15 atoms including one Ni$^{2+}$ ion and surrounding atoms in its vicinity (see Fig. 10). There “colored” atoms are allowed to vibrate, while all other “reservoir” atoms shown in gray are assumed (as an approximation) to have infinite masses: either because some of them are heavy trifluoromethyl CF$_3$ groups, or because other atoms are bound to the surface. Such an approximation provides us with a set of 45 well-defined vibrational frequencies $\omega_{\mu}$.

Further, we consider the wave function $\psi_K$ [Fig. 10(b)], which dominates in the scattering channel responsible for the Kondo effect (essentially, $\psi_K$ is one of those single-occupied
molecular orbitals depicted as $a$ and $a'$ in Fig. 9, which strongly hybridize with the Cu surface [77]. We have computed electron-phonon coupling matrix elements $\lambda'^{a}$, involving the orbital $\psi_X$ and molecular vibrations, which are localized within the same active subspace (for computational details, see Supplemental Material [35], Sec. III).

Our results are presented in Fig. 10 in which we show the dimensionless electron-phonon coupling constants $g = (\lambda'/\hbar \omega_0)^2$ limited to the low-energy excitations. We observe only three eigenmodes (25.1, 32.6, and 33.4 meV) with nonzero coupling constants and frequencies in the proximity of $\delta E \approx 30$ meV. Furthermore, we show in the Supplemental Material [35], Sec. III, that the eigenmodes involve vibrations of Ni$^{2+}$ ions. Their energies will be renormalized when coupled to a continuum of vibrational modes of the macroscopic system, including remaining functional groups of the molecular complex and the Cu surface. However, our additional calculations show that, for example, interaction between two Ni subsystems introduces a moderate splitting of the frequencies only, around $\sim 0.5$ meV. Thus, we argue that three vibrational eigenmodes may rationalize the observation of satellites in $dI/dU$ as a signature of the phonon-assisted Kondo effect.

V. CONCLUSION

To summarize, low-temperature STS measurements on binuclear metal-organic complexes, Ni$_2$ and Mn$_2$, deposited on a Cu(001) surface revealed that the systems undergo the Kondo effect with the Kondo resonances located nearby transition-metal atoms. The relatively large Kondo temperatures, of the order of $\sim 10$ K, were found to depend on the adsorption type. The situation was intriguing here, because the synthesized molecules do not have predefined anchoring groups, which could be responsible for a formation of the chemical bond with the Cu surface [34].

We rationalized experimental observations by performing extensive density functional theory calculations. We searched for the adsorption geometries, where molecules are chemisorbed on the surfaces. In case of Ni$_2$, our simulations show that some STM images (Ni$_2$-$\beta$) can be attributed to a distorted Ni$_2$ complex with partially weakened internal chemical bonds, while other STM images (Ni$_2$-$\alpha$) may be interpreted as arising from molecular fragmentation. In both cases, our calculations suggest a picture of the underscreened ($S = 1$)-type Kondo effect emerging from the open 3d shells of the individual Ni$^{2+}$ ions. Furthermore, theoretical analysis points out that the satellites in the STS spectra observed nearby the zero-bias resonance are likely a signature of the low-energy vibrational excitations of the Ni$_2$ complex and associated with that phonon-assisted Kondo effect.

In broader terms, binuclear complexes present an excellent playground for studying fundamental aspects of magnetic two-impurity (or double quantum dot) systems. By functionalizing the bridging unit it could be possible to enhance the superexchange interaction between two centers, thus allowing us to access different regions of the phase diagram of the double impurity model [73,78,79]. On the applied level, understanding interaction between the spins residing on different functional units is vital to quantum information storage and processing with molecules assembled on surfaces. Our work provides an important step in this direction and identifies further challenges. Apart from the appealing enhancement of the superexchange, the substitution of Ising-like spins (such as Tb) may offer means to study a “double molecular magnet.” As demonstrated here, first-principles calculations will play an indispensable role in this effort.

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[1] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, and H. v. Löhneysen, Phys. Rev. Lett. 88, 176804 (2002).
[2] M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänsch, F. Weigend, F. Evers, H. B. Weber, and M. Mayor, Proc. Natl. Acad. Sci. USA 102, 8815 (2005).
[3] J. Park, A. N. Pasapathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruña, P. L. McEuen, and D. C. Ralph, Nature (London) 417, 722 (2002).
[4] S. Kubatkin, A. Danilov, M. Hjort, H. Cornil, J.-L. Brédas, N. Stuhr-Hansen, P. Hedegård, and T. Bjørnholm, Nature (London) 425, 698 (2003).
[5] E. A. Osorio, K. O’Neill, N. Stuhr-Hansen, F. Nielsen, T. Bjørnholm, and H. S. J. van der Zant, Adv. Mater. 19, 281 (2007).
[6] E. Lörtscher, J. W. Ciszek, J. Tour, and H. Riel, Small 2, 973 (2006).
[7] V. Meded, A. Bagrets, A. Arnold, and F. Evers, Small 5, 2218 (2009).
[8] S. Schmaus, A. Bagrets, Y. Nahas, T. K. Yamada, A. Bork, M. Bowen, E. Beaurepaire, F. Evers, and W. Wulfhekel, Nat. Nanotechnol. 6, 185 (2011).
[9] A. Bagrets, S. Schmaus, A. Jaafar, D. Krämczynski, T. K. Yamada, M. Alouani, W. Wulfhekel, and F. Evers, Nano Lett. 12, 5131 (2012).
[10] P. Gütlich, Y. Garcia, and H. A. Goodwin, Chem. Soc. Rev. 29, 419 (2000).
[11] V. Meded, A. Bagrets, K. Fink, R. Chandrasekar, M. Ruben, F. Evers, A. Bernard-Martel, J. S. Seldenthuis, A. Beukman, and H. S. J. van der Zant, Phys. Rev. B 83, 245415 (2011).
[12] I. Beljakov, V. Meded, F. Symalla, K. Fink, S. Shallcross, M. Ruben, and W. Wenzel, Nano Lett. 14, 3364 (2014).
[13] J. Li, W.-D. Schneider, R. Berndt, and B. Delley, Phys. Rev. Lett. 80, 2893 (1998).

[14] V. Madhavan, W. Chen, T. Jamneala, M. F. Crommie, and N. S. Wingreen, Science 280, 567 (1998).

[15] H. C. Manoharan, C. P. Lutz, and D. M. Eigler, Nature (London) 403, 512 (2000).

[16] N. Knorr, M. A. Schneider, L. Diekhöner, P. Wahl, and K. Kern, Phys. Rev. Lett. 88, 096804 (2002).

[17] N. Néel, J. Kröger, L. Limot, K. Palotas, W. A. Hofer, and R. Berndt, Phys. Rev. Lett. 98, 016801 (2007).

[18] D. Ehm, S. Hüfner, S. F. Reintert, J. Kroha, P. Wölle, O. Stockert, C. Geibel, and H. v. Löhneysen, Phys. Rev. B 76, 045117 (2007).

[19] L. Gao, W. Ji, Y. B. Hu et al., Phys. Rev. Lett. 99, 106402 (2007).

[20] Y.-S. Fu, S.-H. Ji, Xi Chen et al., Phys. Rev. Lett. 99, 256601 (2007).

[21] I. Fernández-Torrente, K. J. Franke, and J. I. Pascual, Phys. Rev. Lett. 101, 217203 (2008).

[22] U. G. E. Perera, H. J. Kulik, V. Iancu, L. G. G. V. Dias da Silva, S. E. Ulloa, N. Marzari, and S.-W. Hla, Phys. Rev. Lett. 105, 106601 (2010).

[23] J. Nygård, D. H. Cobden, and P. E. Lindelof, Nature (London) 408, 342 (2000).

[24] J. Paaske, A. Rosch, P. Wölle, N. Mason, C. M. Marcus, and J. Nygård, Nat. Phys. 2, 460 (2006).

[25] Single molecule magnets (SMMs) have attracted a lot of interest [26,27] recently. For example, magnetic relaxation time of SMMs could be years at low temperatures that has been observed in bulk crystals [28,29]. Potential applications of SMMs, e.g., as high-density data storage units, are envisaged. For that, individual SMMs could be years at low temperatures that has been observed in bulk crystals [28,29]. Potential applications of SMMs, e.g., as high-density data storage units, are envisaged.

[26] D. Gatteschi and R. Sessoli, Angew. Chem. Int. Ed. 42, 268 (2003).

[27] L. Bogani and W. Wernsdorfer, Nat. Mater. 7, 179 (2008).

[28] G. Christou, D. Gatteschi, D. N. Hendrickson, and R. Sessoli, Mater. Res. Soc. Bull. 25, 66 (2000).

[29] M. Cavallini, M. Facchini, C. Albonetti, and F. Biscarini, Phys. Chem. Chem. Phys. 10, 784 (2008).

[30] J. Gómez-Segura, I. Díez-Pérez, N. Ishikawa, M. Nakano, J. Veciana, and D. Ruiz-Molina, Chem. Commun. 27, 2866 (2006).

[31] L. Vitali, S. Fabris, A. M. Conte, S. Brink, M. Ruben, S. Baroni, and K. Kern, Nano Lett. 8, 3364 (2008).

[32] S. Kahle, Zh. Deng, N. Malinowski, Ch. Tonnor, A. Forment-Aliaga, N. Thontases, G. Rinke, D. Le, V. Turkowski, T. S. Rahman, S. Rauschenbach, M. Ternes, and K. Kern, Nano Lett. 12, 518 (2012).

[33] W. Liang, M. P. Shores, M. Bockrath, J. R. Long, and H. Park, Nature (London) 417, 725 (2002).

[34] S. Wagner, F. Kisslinger, S. Ballmann, F. Schramm, R. Chandrasekar, T. Bodenstein, O. Fuhr, D. Secker, K. Fink, M. Ruben, and H. B. Weber, Nat. Nanotechnol. 8, 575 (2013).

[35] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.91.195424 for details of electronic structure calculations and synthesis of molecular complexes, which includes Refs. [36–45].
[62] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009).
[63] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[64] A. Arnold, F. Weigend, and F. Evers, J. Chem. Phys. 126, 174101 (2007).
[65] J. Wilhelm, M. Walz, M. Stendel, A. Bagrets, and F. Evers, Phys. Chem. Chem. Phys. 15, 6684 (2013).
[66] T. Jamneala, V. Madhavan, W. Chen, and M. F. Crommie, Phys. Rev. B 61, 9990 (2000).
[67] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[68] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys.: Condens. Matter 9, 767 (1997).
[69] S. Kümmler and L. Kronik, Rev. Mod. Phys. 80, 3 (2008).
[70] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
[71] A. Bagrets, J. Chem. Theory Comput. 9, 2801 (2013).
[72] Our calculations indicate that a fractional charge of $\approx 0.5e$ leaks out from the surface to the molecule, populating partially the LUMO of the Ni$_2$ complex and the LUMO* of the bpym moiety (see Fig. 9). Also, a magnetic moment carried by the complex is slightly reduced, from $4.0\mu_B$ (gas-phase molecule) down to $3.3\mu_B$.
[73] C. Jayaprakash, H. R. Krishna-murthy, and J. W. Wilkins, Phys. Rev. Lett. 47, 737 (1981).
[74] We remind that DFT with a quasilocal XC functional does not allow us to recover a Kondo resonance at the Fermi level.
[75] J. J. Parks, A. R. Champagne, T. A. Costi, W. W. Shum, A. N. Pasupathy, E. Neuscamman, S. Flores-Torres, P. S. Cornaglia, A. A. Aligia, C. A. Balseiro, G. K.-L. Chan, H. D. Abriüna, and D. C. Ralph, Science 328, 1370 (2010).
[76] J. Paaske and K. Flensberg, Phys. Rev. Lett. 94, 176801 (2005).
[77] More specifically, “Kondo-active” molecular orbitals (MOs) depicted as $a$ and $a'$ in Fig. 9, which are strongly coupled to the Cu surface, are well approximated by symmetric and antisymmetric combinations $\psi^{\pm}_{k} = \frac{1}{\sqrt{2}}(\phi_{b1}^{\uparrow} \pm \phi_{a2}^{\uparrow})$ of the single-occupied MOs of the distorted Ni$_2$ complex with $C_{2v}$ symmetry. Here $b_1$ and $a_2$ refer to irreducible representations of the $C_{2v}$ group, with $b_1$ being even and $a_2$ being odd with respect left-right reflection $\sigma_v$.
[78] W. Hofstetter and H. Schoeller, Phys. Rev. Lett. 88, 016803 (2001).
[79] J. Bork, Y.-h. Zhang, L. Diekhöner, L. Borda, P. Simon, J. Kroha, P. Wahl, and K. Kern, Nat. Phys. 7, 901 (2011).