SUPPORTING INFORMATION FOR

Ligand Mediated Evolution of Size Dependent Magnetism in Cobalt Nanoclusters

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Optimized structures



Figure S1. Structures of Co_N clusters



Figure S2. Structures of Co_NCl_Y clusters



H

Figure S4. Structures of clusters with ligand shell composed of both Cl and PH₃



Figure S5. Structures of $Co_{20}L_M$ clusters with different percent ligand coverages



Figure S6. Structures of $Co_{45}L_M$ clusters with different percent ligand coverages

Impact of multiple component ligand shells on the magnetic properties of \mbox{Co}_N nanocluster cores

Many nanoclusters that are synthetically accessible with fewer than 100 metal atoms contain multiple component ligand shells, where each type of ligand is important for the stability of the nanocluster.¹⁻³ Structural diversity on the surface often arises due to having many components in the solution at the time of nucleation, and a high energy surface that will bind to many different ligands to gain both thermodynamic and kinetic stability. To extend our work toward more realistic model systems, we built a set of clusters with both Cl and PH₃ ligands present (Figure S4). The Cl ligands were added to bare surface sites of the Co_N(PH₃)_Z set of ligands and subsequently reoptimized. Overall, 9 Co_NCl_Y(PH₃)_Z clusters were considered and together, 7 unique surface coordination environments were generated by the ligand shell after optimization (Figure S7A). Here a unique environment was defined as either having a coordination number to each Cl and PH₃ ligands (i.e. 1Cl/1PH₃ vs. 2Cl/PH₃), or as having the coordinating ligand binding to a different number of surface atoms (i.e. direct binding vs. bridging 2 Co atoms).

In bare clusters and single component ligand shells, we find a clear correlation between the composition of the immediate coordination environment at a surface Co atom and its LMM, allowing us to isolate the role the ligand plays on the electronic structure at the surface. Consistent with these observations with single component ligand shells, as the Co-Co coordination number increases in the dual component ligand shells a general quenching of the LMM is observed, independent of the ligand coordination. However, coordination environments containing both Cl and PH₃ ligands present show LMMs that fall between what is expected based on results form single component ligand shells. LMM averaging leads to the total magnetic moment of the dual ligand shell clusters falling between that of the pure Cl and PH₃ ligand shells for a given core size (Figure S1B). Importantly, the $Co_N Cl_Y (PH_3)_Z$ clusters does not qualitatively differ from the pure ligand shells, where there is no size dependent evolution of magnetism. The lack of size dependence indicates that the local coordination environment remains the determining factor in the LMM in complex ligand shells, and the set of coordination environments on a given nanocluster will determine the overall magnetism of a given system.



Figure S7: A) Each unique local structural motif generated from ligand shell in $Co_NCl_Y(PH_3)_Z$ clusters. The number below each structure indicates the LMM of the center of coordination environment (blue atom). B) Average LMM on each Co atom as a function of number of atoms in the core of each cluster considered including dual ligand shell systems. C) LMM as a function of Co-Co coordination number for every atom in each cluster considered in this study.

Calculation of total and local magnetic moments

The local magnetic moment atom i is given by the following equation.⁴

$$\mu_i = \int_0^R [\rho_{\uparrow}(r) - \rho_{\downarrow}(r)] dr$$

Where R is the radius of the augmentation sphere centered at atom i, and $\rho_{\uparrow}(r)$ ($\rho_{\downarrow}(r)$) is the majority (minority) spin density. The radius of the augmentation sphere in which the integration is preformed is chosen as half the bond length of the nearest neighbor bond length to ensure there is no overlap between atoms. The total magnetic moment of the system is given by the sum of each atoms local magnetic moment.

To estimate the error in the calculation of total magnetic moment we report the value of spin contamination in **Figure S11**. The total magnetic moment is calculated as an integral of the net spin density over all space. In an unrestricted calculation, the spatial components of the spin-up and spin-down wave functions can be different. Spatial mismatch results in regions of space where the net spin density is negative. In DFT, spin contamination is calculated as the integral of the net spin density over all space where the spin down electron density is greater than the spin up electron density.⁵

Coordination Number

In order to characterize the local atomic structure of each cluster and correlate this structure with local magnetism of a given position in the cluster we utilize the coordination number of a given atom position extensively. Because the average Co-Co bond lengths are different for each cluster, both as a function of size and ligand shell composition (Figure S8), it is difficult to assign whether or not a bond exists between two atoms. To calculate coordination numbers consistently across each cluster, we calculated a fractional coordination number given below:

$$C_i = \sum_{j=1}^N C_{ij}$$

Where,

$$C_{ij} = \begin{cases} 1 & \text{, if } r_{ij} \leq r_{eq} \\ \exp\left(-\left(\frac{r_{ij} - r_{eq}}{\sigma}\right)^2\right) & \text{, otherwise} \end{cases}$$

First we calculate every bond length between each pair of Co atoms less than 3.0 Å apart. From this set of bond lengths we calculate the average (r_{eq}) and the standard deviation (σ) . The coordination number of atom i is given by equation 1, where we calculate the distance between atom i and atom j (r_{ij}) , if this value is less than the equilibrium BL we add one to the coordination number, if it is greater than the equilibrium BL the value is weighted with a Gaussian distribution.

Ligand binding energy

The ligand binding energy (LBE) of each Co_N (N = 15 - 55) cluster was calculated using the following equation.

$$LBE = E[Co_{N}(Lig)_{M}] - (E[Co_{N}] + M * E[Lig])$$

Where M is the number of ligands in the cluster. In cases where the ligand has an unpaired electron and is therefore not stable as a radical (i.e. Cl), the hydrogenated version of the ligand was used to calculated E[Lig] and the LBE was calculated with the following modified version of the above equation.

$$LBE = \left(E[Co_{N}(Lig)_{M}] + \frac{M}{2} * E[H_{2}]\right) - \left(E[Co_{N}] + M * E[Lig]\right)$$



Figure S8. Average Co-Co BL as a function of nanocluster core size.



Figure S9 Average LMM as a function of the average Co-Co bond length for each ligand shell composition.



Figure S10. Average LBE as a function of core size.



Figure S11. Percent spin contamination present in calculating as a function of nanocluster core size.



Figure S12. Local magnetic moment as a function of atomic charge for every Co atom in each nanocluster considered.



Figure S13. Average Co-Co bond length in the first coordination environment as a function of the local magnetic moment for every Co atom in each nanocluster considered.

System	0.5	1.0	1.5	2.0
Co ₃₅ Cl ₁₅	67.9	67.9	67.9	67.9
Co ₃₅ (PH ₃) ₁₈	54.7	54.7	54.7	54.7
Co ₃₅ (PH ₃) ₁₈ Cl ₁₀	60.2	60.2	60.2	60.2

Table S1. Various starting local magnetic moments (LMMs) used on each atom to initiate single point calculation and resulting total magnetic moment (TMM) for each ligand shell considered for Co_{35} core size.

References

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