Supplementary Information for

Effect of coverage on the magnetic properties of -COOH, -SH, and -NH₂ ligand-protected cobalt nanoparticles

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This document contains supplementary information in the form of tables and figures for a complete insight into the performed calculations of the magnetic properties of bare and ligand-protected cobalt nanoparticles.

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Computational details

Bulk

Bulk calculations were conducted on an hcp cell (P63/mmc space group) containing two cobalt atoms and an fcc cell (Fm3m space group) with four cobalt atoms (taken from Wyckoff crystal structures¹), both of which were fully relaxed until the assigned accuracy was reached. Calculations were carried out in reciprocal space with varying number of k-points until the satisfactory convergence has been reached at a k-point mesh of $17\times17\times9$ for hcp and $8\times8\times8$ for fcc Co. The conjugate gradient technique, with a force convergence criterion of 1.0×10^{-2} eV/Å, has been used to perform geometry optimisations.

NPs

Experimental studies have shown that transition metal NPs can either have regular phase ordering and exist as face-cantered cubic (fcc), body-centred cubic (bcc), or hexagonal close-packed (hcp) crystals, or they can comprise several twinned fcc crystallites.² Former are known as crystalline NP morphologies, and they are constructed by terminating their respective bulk phases with the most stable Miller index surfaces at appropriate distances from the chosen centre atom based on the Gibbs-Wulff theorem.³ Truncations with higher index facets are known to provide further stabilisation of NP shapes by optimising surface-to-volume ratio. From fcc bulk, one can therefore obtain a simple cube with (100) facets, an octahedron by using solely (111) facets, truncated octahedron by introducing six (100) facets along the six vertices of octahedron, or cuboctahedron by introducing (111) cuts along the eight vertices of a simple cube. Starting form an hcp bulk and cutting in the (1011) direction, obtained shape is a hexagonal bipyramid, which can be truncated by two (0001) facets, one at the tip of each pyramid. Irregular icosahedral and decahedral twinned shapes are known as non-crystalline motifs, and they are characterised by a five-fold symmetry and constructed through symmetry operations. An icosahedral NP is built by packing together twenty fcc tetrahedra with (111) closepacked facets as their base and a central vertex as their apex conjoined at 12 boundary vertices⁴, while decahedral NP is obtained by packing five tetrahedra so that they have a common edge.⁵ Former can be truncated by five (100) facets, yielding an Ino decahedron, while further truncation at vertical edges by ten re-entrant (111) facets gives a Marks decahedron.^{6,7}

Geometry optimisations were carried out without any constraints, with the convergence criteria for the change in the total energy and interatomic forces between two steps of 1.0×10^{-6} and 1.0×10^{-2} eV/Å. The vacuum space in the unit cell was set to be more than 12 Å in each direction to avoid interactions with the periodic images.

VESTA⁸ and USCF Chimera⁹ were used for visualisation and analysis.

Orbital moments and magnetic anisotropy of Co NPs

Calculated MAE energies are compared to experimental results conducted on Co truncated octahedral of increasing sizes in Figure S1. Correlated Néel pair modelling of the (100) and (111) fcc Co surfaces shows that the addition of a single facet decreases the general enhancement in magnetic anisotropy for larger particles. Nevertheless, it is still possible to obtain high MAE values, as measured by experiment, probably because of the shape induced anisotropy. This means that notably polycrystallinity, which is expected in large particles due to the fabrication mechanism, plays an important role in reducing the contributions of crystal-symmetry breaking to the global anisotropy. Defects have, on the other hand, been proposed as being responsible for uniaxial anisotropy in larger cobalt or iron mNPs (8–20 nm).^{10,11} Detailed comparison of DFT obtained values and experimental data is given in the main article.



Figure S1 DFT predicted magnetic anisotropy energies for Co NPs of varying diameters and morphologies in comparison with experimental and Néel pair (100) – full line and (111) – dashed line surface correlated values. Experimental and Néel pair modelling results are taken from ¹².



Figure S2 Average orbital moments, L_x and L_z , for cobalt NPs of different morphologies as a function of the shell of neighbours. In all cases, L_x and L_z correspond to the hard and easy magnetisation axes. Dotted lines are to guide an eye only.

Characterisation of differently shaped Co NPs based on their average local orbital moments is shown in Figure S2 as a function of neighbour shells. Shells of neighbours were identified with respect to the radial distance from the central atom. In general, and in agreement with previous studies^{13,14}, the values of L_i are in most cases enhanced with respect to those of the fcc and hcp cobalt bulk, which are 0.071 and 0.074 μ_B per Co atom, respectively. Considering the difference between the two orientations, the hcp geometry showed the largest deviation amongst the crystalline shapes, while for fcc morphologies there is almost no distinction in L_x and L_z for each shell, and this lack of variance is also present in the icosahedron. Decahedra experience notable oscillations between positive and negative ΔL values. These alternations within the shell-decomposed orbital moments of varying morphologies are indicators of a complex behaviour of the local magnetic anisotropy in electronic energy, L_z - $L_x \propto E_z$ - E_x ¹⁵, and hence they give an anticipation on differences in total MAEs. The results clearly indicate the role of geometrical parameters in the magnetic behaviour of cobalt NPs.

Binding sites over Co NPs

Figure S3 shows possible binding sites for ligands on 55-atom icosahedron and 57-atom hcp Co NPs. To achieve the most favourable binding on one of twenty (111) facets of the icosahedron, molecules which interact with two surface Co atoms (-COOH and -NH₂ ligands) bind vertex-edge Co-Co pair (shown in blue). After vertex-edge pairs have been saturated at high ligand coverages, further ligand molecules are limited to bind in the only other option which remains available – two Co atoms positioned on different edges of the (111) facet (shown in red). Thiol molecules require three Co atoms per ligand, and stronger binding is established for edge-vertex-edge combinations (shown in blue) compared to the three edge Co atoms interaction which positions the molecule in the centre of the (111) facet (shown in red). Facets exposed on the surface of hcp clusters in addition to edge and vertex atoms also contain central atoms with higher coordination numbers. When those atoms interact with the ligand molecule, the adsorption energy released is significantly reduced (shown in red).



Figure S3 Different binding positions and their respective interaction strength for various ligands and facets on 55-atom icosahedral (left panel) and 57-atom hcp (right panel) cobalt NPs.

Atom-decomposed electronic and magnetic properties

The relationship between the local magnetic moments, LMM, of differently passivated NPs is captured in Figure S4 as a function of the coordination numbers of Co atoms, CN. In unpassivated NPs, there is little dependence of the local magnetic moment on the position of the atom within the specific segment of the NP (core, inner, and surface segment). The distribution of LMM across segments is governed by the CNs of cobalt atoms, and consequently, the average spacing between d-band energy levels. Discernible deviation from these grouped LMMs is captured for each passivation case. In particular, both hcp and icosahedron NPs passivated by carboxylic acid ligands see an enhancement in the LMMs of surface based cobalt atoms. The change is less prominent for the atoms exempted from the direct interaction with the ligands, whose magnetic moments slightly decreased, except for the central atom of the hcp NP which experienced an increase of 0.40 μ_B . Amine and thiol ligands show opposite behaviour. Passivation by amine is followed by a substantial drop in the LMMs of many cobalt atoms in all segments of the NP, although about one third of surface atoms showed an increase in the magnetic moments. The decline is even more pronounced for the thiol-protected icosahedral NP, where only a handful of the 55 atoms did not lose magnetic moment compared to their unpassivated LMM values.



Figure S4 Atom decomposed local magnetic moments, LMM, as a function of Co–Co coordination numbers, CN, for bare and ligand-passivated hcp and icosahedral cobalt NPs.

Atomic charges and spin magnetic moments were decomposed as a function of the segments of the NPs for each ligand coverage of the icosahedron in Tables S1-S3 and the hcp NP in Table S4.

Table S1 Magnetic properties and Bader charge analysis of systems with a Co55 icosahedral core and different
carboxylic acid coverages in % as a function of position in the NP. Magnetic moments are in μ_B and charges in
e ⁻ .

	total	centre	average	average	total	centre	average	average
	magnetic	atom	inner	surface	core	atom	inner	surface
coverage	moment	LMM	LMM	LMM	charge	charge	charge	charge
0	100.118	1.715	1.701	1.857	0.27	-0.137	0.034	-0.004
10	99.235	1.542	1.679	1.796	1.60	-0.178	0.046	0.028
20	99.393	1.483	1.666	1.800	2.95	-0.183	0.040	0.062
30	100.457	1.449	1.663	1.818	4.95	-0.191	0.033	0.112
40	100.608	1.443	1.657	1.819	6.28	-0.186	0.032	0.144
50	101.058	1.310	1.653	1.831	7.55	-0.194	0.028	0.176
60	101.025	1.306	1.622	1.832	8.86	-0.195	0.024	0.208
70	101.313	1.316	1.607	1.836	10.16	-0.201	0.018	0.241
80	102.983	1.454	1.635	1.864	11.48	-0.205	0.013	0.274
90	103.126	1.540	1.616	1.870	12.72	-0.198	0.001	0.307
100	103.318	1.590	1.590	1.879	13.94	-0.207	-0.006	0.339

Table S2 Magnetic properties and Bader charge analysis of systems with a Co55 icosahedral core and different amine coverages in % as a function of position in the NP. Magnetic moments are in μ_B and charges in $|e^-|$.

	total	centre	average	average	total	centre	average	average
	magnetic	atom	inner	surface	core	atom	inner	surface
coverage	moment	LMM	LMM	LMM	charge	charge	charge	charge
0	100.118	1.715	1.701	1.857	0.27	-0.137	0.034	-0.004
10	100.571	1.649	1.707	1.821	1.17	-0.145	0.056	0.010
20	99.325	1.514	1.675	1.794	2.10	-0.195	0.029	0.041
30	98.776	1.489	1.637	1.767	3.20	-0.166	0.026	0.064
40	99.098	1.515	1.671	1.809	4.52	-0.174	0.017	0.102
50	98.606	1.554	1.675	1.804	5.54	-0.184	0.020	0.126
60	98.312	1.540	1.645	1.774	6.51	-0.181	0.018	0.150
70	96.792	1.570	1.630	1.738	7.55	-0.164	0.028	0.175
80	96.639	1.577	1.644	1.732	8.60	-0.190	0.023	0.202
90	96.670	1.459	1.592	1.741	9.77	-0.184	0.018	0.231
100	95.057	1.543	1.565	1.707	10.55	-0.175	0.010	0.252

	total	centre	average	average	total	centre	average	average	
	magnetic	atom	inner	surface	core	atom	inner	surface	
coverage	moment	LMM	LMM	LMM	charge	charge	charge	charge	
0	100.118	1.715	1.701	1.857	0.27	-0.137	0.034	-0.004	
14	100.536	1.603	1.712	1.817	1.18	-0.159	0.040	0.016	
21	97.664	1.415	1.668	1.747	1.50	-0.171	0.038	0.020	
29	97.344	1.391	1.665	1.741	1.97	-0.190	0.035	0.036	
43	96.804	1.399	1.679	1.753	3.16	-0.185	0.032	0.070	
50	96.772	1.469	1.659	1.740	3.45	-0.183	0.025	0.074	
64	95.052	1.469	1.652	1.700	4.43	-0.181	0.030	0.096	
78	93.446	1.340	1.633	1.670	5.50	-0.191	0.025	0.123	
93	93.454	1.327	1.635	1.662	6.79	-0.198	0.043	0.157	
100	94.180	1.369	1.654	1.676	7.09	-0.187	0.040	0.161	

Table S3 Magnetic properties and Bader charge analysis of systems with a Co55 icosahedral core and different thiol coverages in % as a function of position in the NP. Magnetic moments are in μ_B and charges in $|e^-|$.

Table S4 Magnetic properties and Bader charge analysis of systems with a Co57 hcp core and different carboxylic acid coverages in % as a function of position in the NP. Magnetic moments are in μ_B and charges in $|e^-|$.

	total	centre	average	average	total	centre	average	average
	magnetic	atom	inner	surface	core	atom	inner	surface
coverage	moment	LMM	LMM	LMM	charge	charge	charge	charge
0	96.179	1.215	1.538	1.732	0.29	-0.020	0.033	-0.003
10	98.008	1.243	1.543	1.726	1.55	-0.045	0.029	0.027
20	100.391	1.428	1.572	1.764	3.53	-0.026	0.025	0.073
30	100.666	1.397	1.565	1.768	4.88	-0.033	0.021	0.105
40	102.451	1.442	1.594	1.795	6.25	-0.045	0.016	0.137
50	102.598	1.489	1.583	1.797	7.54	-0.040	0.011	0.168
60	102.912	1.493	1.577	1.803	8.84	-0.038	0.008	0.199
70	103.784	1.544	1.605	1.830	10.14	-0.044	0.004	0.229
80	104.093	1.567	1.558	1.822	11.89	-0.026	-0.005	0.267
90	104.189	1.573	1.553	1.824	13.11	-0.040	-0.011	0.299
100	104.137	1.532	1.541	1.826	14.38	-0.032	-0.011	0.330

Structural properties

100

2.366

2.480

Average Co-Co distances for atoms within the same segment and between the different segments (centre-inner and inner-surface atom distances), as well as the distances and angles between the functional group atoms of the ligands and bonding surface Co atoms are summarised in Tables S5-S7 for passivated icosahedra and in Table S8 for carboxylic acid-protected hcp Co NPs.

innersurfacesurface-Co-Co-O centreinnersurface coverage inner inner surface ligand angle 0 2.357 2.480 2.350 2.468 --10 86.209 2.366 2.490 2.354 2.471 1.949 20 2.367 2.500 2.362 2.463 1.960 86.312 30 2.379 86.124 2.366 2.489 2.468 1.956 40 2.368 2.485 2.389 2.471 1.954 86.855 50 2.474 2.467 1.946 85.906 2.363 2.381 60 2.368 2.488 2.379 2.460 1.956 86.612 70 2.370 2.510 2.384 2.465 1.945 86.421 80 2.499 2.382 2.474 1.953 86.593 2.369 90 2.368 2.480 2.391 2.490 1.964 86.544

Table S5 Average Co-Co distance, bond lengths, and angles formed between surface Co atoms and carboxyl head group. All distances are in Å and angles in °.

Table S6 Average Co-Co distances, bond lengths and angles formed between surface Co atoms and amine head group. All distances are in Å and angles in °.

2.406

2.472

1.953

86.342

	centre-	inner-	inner-	surface-	surface-	Co-N-Co
coverage	inner	inner	surface	surface	ligand	angle
0	2.357	2.480	2.350	2.468	-	-
10	2.358	2.481	2.362	2.469	1.969	75.397
20	2.353	2.475	2.369	2.479	1.968	75.173
30	2.348	2.468	2.358	2.474	1.968	75.155
40	2.354	2.475	2.373	2.479	1.977	75.045
50	2.352	2.474	2.373	2.473	1.976	74.805
60	2.354	2.475	2.370	2.456	1.972	74.518
70	2.351	2.473	2.378	2.467	1.974	74.283
80	2.355	2.476	2.390	2.473	1.976	74.082
90	2.353	2.476	2.398	2.473	1.984	73.832
100	2.353	2.476	2.396	2.474	1.979	73.600

	centre-	inner-	inner-	surface-	surface-	Co-S-Co
coverage	inner	inner	surface	surface	ligand	angle
0	2.357	2.480	2.350	2.468	-	-
14	2.358	2.479	2.357	2.478	2.228	72.068
21	2.351	2.472	2.364	2.475	2.207	72.265
29	2.355	2.475	2.358	2.477	2.211	71.854
43	2.358	2.479	2.370	2.473	2.215	71.959
50	2.351	2.468	2.367	2.476	2.226	71.758
64	2.359	2.481	2.370	2.472	2.208	72.211
78	2.355	2.472	2.378	2.470	2.215	71.707
93	2.357	2.476	2.387	2.478	2.219	72.234
100	2.359	2.479	2.382	2.477	2.221	72.038

Table S7 Average Co-Co distances, bond lengths and angles formed between surface Co atoms and thiol head group. All distances are in Å and angles in °.

Table S8 Average Co-Co distances, bond lengths and angles formed between surface Co atoms and carboxyl head group. All distances are in Å and angles in °.

	centre-	inner-	inner-	surface-	surface-	Co-Co-O
coverage	inner	inner	surface	surface	ligand	angle
0	2.449	2.453	2.392	2.402	-	-
10	2.440	2.441	2.411	2.408	1.914	86.392
20	2.442	2.450	2.389	2.414	1.933	86.115
30	2.442	2.444	2.403	2.415	1.932	86.060
40	2.440	2.438	2.409	2.425	1.935	85.699
50	2.441	2.451	2.412	2.418	1.957	85.896
60	2.441	2.442	2.404	2.428	1.946	86.430
70	2.443	2.439	2.420	2.432	1.950	86.792
80	2.446	2.448	2.419	2.436	1.952	86.052
90	2.438	2.438	2.423	2.442	1.945	86.393
100	2.434	2.432	2.422	2.433	1.959	86.407

Densities of state, DOS

Figure S5 shows densities of state for a single pair of carboxylic acid molecule interacting with the surface Co atoms of the (0001) and $(10\overline{1}1)$ facets of the 57-atom hcp Co NP.



Figure S5 Projected densities of state, DOS, for a single molecule of acetic acid interacting with a (0001) surface (top panel) and a $(10\overline{1}1)$ surface (bottom panel) of the 57-atom hcp Co NP. Both majority and minority spins are shown. DOS of the surface Co atoms interacting with the molecule are shown as filled blocks, while DOS of the inner Co atom directly beneath the interaction site are shown as dotted lines.

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