

Chemical Control of Structural and Magnetic Properties of Cobalt Nanoparticles

Olivier Margeat,[†] Catherine Amiens,^{*,†} Bruno Chaudret,[†] Pierre Lecante,[‡] and Robert E. Benfield[§]

Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077 Toulouse Cedex 04, France, Centre d'Elaboration des Matériaux et d'Etudes Structurales, CNRS, 29, Rue Jeanne Marvig, BP 4347, 31055 Toulouse Cedex, France, and Functional Materials Group, School of Physical Sciences, University of Kent, Canterbury CT2 7NR, U.K.

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Oxide-free cobalt nanoparticles (NPs) of 2.5–3 nm diameter have been synthesized in the presence of di-isobutyl aluminum hydride (DiBAH), a potential alumina source, from two different precursors: $\text{Co}(\eta^3\text{C}_8\text{H}_{13})(\eta^4\text{C}_8\text{H}_{12})$ and $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$. The NPs display very different structural and magnetic features, which are related to the difference in chemical environment at the NPs surface.

Tailoring nanoparticles (NPs) surface becomes crucial for controlling their deposition on various substrates, inducing 3D assemblies,^{1,2} ensuring their biocompatibility or forming an airtight shell which would protect the NPs from oxidation. Chemical control of the synthesis of nanometer scale materials also leads to fascinating phenomena such as stabilization of new phases³ and change in electronic and magnetic properties due to strong surface effects related to the coordination of ligands at the NPs surface.^{4,5} These considerations are especially important when considering magnetic NPs for which anisotropy and magnetization depend on structural and electronic properties. Furthermore, anisotropic growth of the NPs is claimed to be controlled via ligand coordination in certain cases.⁶ It is thus crucial to obtain a better knowledge of the surface/ligand interaction.

Our group has long been involved in the synthesis of metal NPs by an organometallic route and more specifically in the study of ligand coordination at the surface of the NPs^{7,8} together with the effect of such a coordination on their structural^{9,10} and magnetic properties.^{11,12} For instance, it has

been shown that platinum NPs could change structure from fcc to icosahedral depending on the phosphine coverage of their surface.¹⁰ We have also shown that adsorption of carbon monoxide at the surface of cobalt NPs embedded in polymer matrices induces a collapse of their magnetization.¹¹ However, such a study is limited to very small molecules able to diffuse through the polymer matrix. Using ligands as stabilizing agents during the NPs synthesis is thus required for further investigations of the relation between the chemical nature of the ligands and their effect on surface magnetism. This has been evidenced in the case of nickel NPs where we showed that donor ligands such as amines do not alter the surface magnetism of the NPs but promote the formation of nanorods as a result of shape control, whereas the use of trioctylphosphine oxide leads to NPs of reduced magnetization.¹³

Here, we report the synthesis, structure, and magnetic properties of cobalt NPs obtained from two different precursors, $\text{Co}(\eta^3\text{C}_8\text{H}_{13})(\eta^4\text{C}_8\text{H}_{12})$ and $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$, in the presence of di-isobutyl aluminum hydride (DiBAH), a commercially available aluminum-based Lewis acid, and compare the results to those obtained when the NPs are synthesized in the commonly used polymer matrix, poly(vinylpyrrolidone) (PVP).^{11,12} An aluminum compound was chosen here because it can be the starting point for the growth of alumina coatings which should display interesting dielectric properties, high thermal conductivity, and possibly prevent air oxidation.¹⁴

When $\text{Co}(\eta^3\text{C}_8\text{H}_{13})(\eta^4\text{C}_8\text{H}_{12})$ was hydrogenated in the presence of 1 equiv of DiBAH,¹⁵ a very stable black colloidal solution was obtained. Well-dispersed NPs of 2.5(±0.4) nm

* Corresponding author. E-mail: amiens@lcc-toulouse.fr.

[†] Laboratoire de Chimie de Coordination.

[‡] Centre d'Elaboration des Matériaux et d'Etudes Structurales.

[§] University of Kent.

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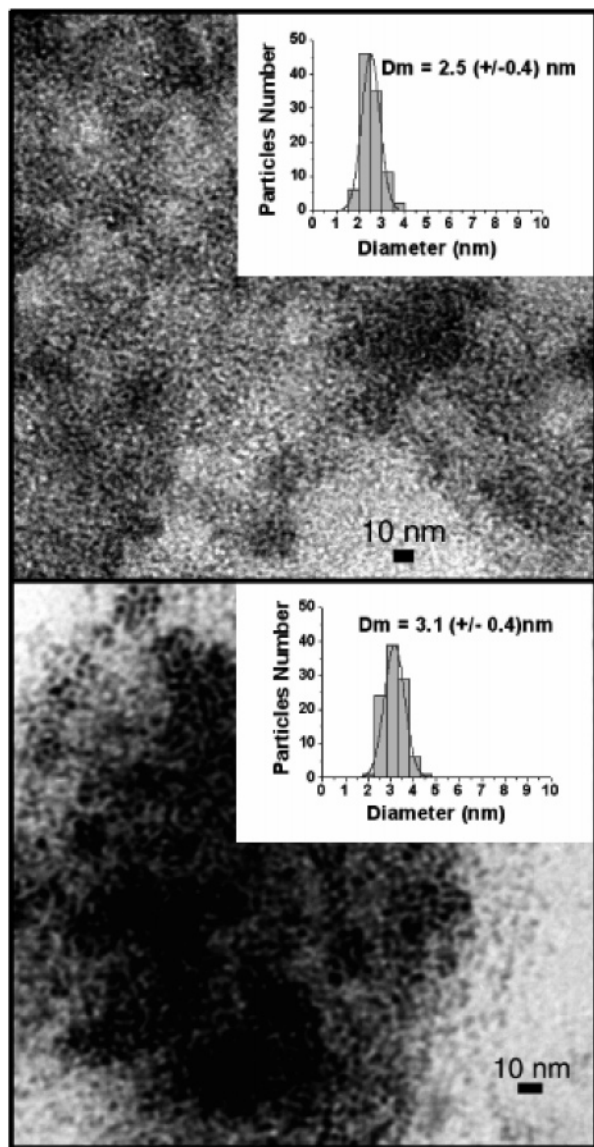


Figure 1. TEM and size distribution of cobalt NPs obtained from (top) $\text{Co}(\eta^3\text{C}_8\text{H}_{13})(\eta^4\text{C}_8\text{H}_{12})$, sample 1; (bottom) $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$, sample 2.

diameter were observed by transmission electron microscopy (TEM) (Figure 1). The NPs were recovered as a black sticky material **1**, which was further characterized by wide-angle X-ray scattering (WAXS), chemical microanalysis, and magnetic measurements on a SQUID magnetometer. The magnetization curve recorded at 2 K displays a hysteretic behavior, with $H_c = 1500$ G (Figure 2) and a magnetization which does not saturate even at high fields (5 T). From the magnetization value at 5 T and the cobalt content in the material (19%), we can calculate an average value of the magnetic moment per cobalt atom: $1.06(\pm 0.05) \mu_B/\text{Co}$. This is very low when compared to the expected bulk value of $1.72 \mu_B/\text{Co}$ and corresponds to a loss of 38% of the magnetization. It is noteworthy that for NPs of this size, the proportion of atoms at the surface is approximately of 50%.

(15) In a typical experiment, 1 mmol of DiBAH dissolved in 10 mL of toluene was added to 1 mmol (276 mg) of $\text{Co}(\eta^3\text{C}_8\text{H}_{13})(\eta^4\text{C}_8\text{H}_{12})$ dissolved in 10 mL of toluene. The resulting dark brown solution was pressurized under 3 bar H_2 at room temperature for 48 h. The black solution is then evaporated to dryness. 242 mg of a black sticky material was recovered. %Co: 19%.

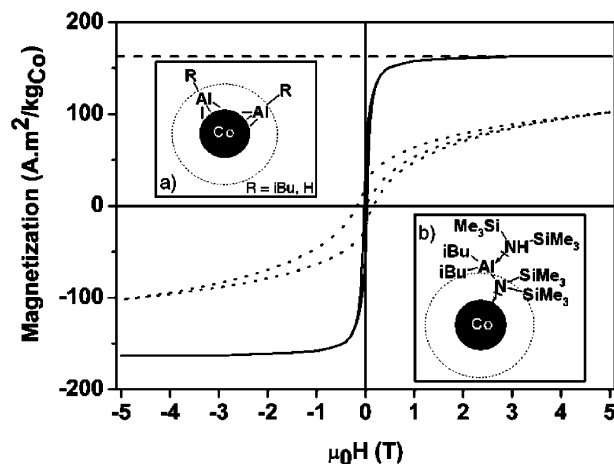


Figure 2. Magnetization curves recorded at 2 K for sample 1 (dotted line) and sample 2 (solid line). The horizontal dashed line represents the saturation magnetization of bulk cobalt. Insets: Schematic representations of the chemical environment of the NPs surface, (a) sample 1; (b) sample 2.

The loss in magnetization corresponds to a partial quenching of the magnetic contribution of the surface. The fact that the magnetization of the surface layer is not completely quenched is best explained by a partial coverage of the surface, in good agreement with the bulkiness of the ligands.

As a comparison, NPs were also synthesized from $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$.¹⁶ This precursor contains amido ligands which can strongly interact with DiBAH and form thermodynamically very stable Al–N bonds. Accordingly, it decomposes spontaneously in the presence of DiBAH. NPs were obtained in this case by a slow addition of DiBAH (2 equiv) on a toluene solution of the cobalt precursor at -50 °C.¹⁷ The initially green solution turns brown and then black when the solution temperature is allowed to rise up to room temperature. TEM investigation of the solution evidences well-dispersed NPs of $3.1(\pm 0.4)$ nm (Figure 1). Careful addition of methanol to this solution afforded a gray solid, **2**, which could be recovered by filtration. The magnetization curve recorded at 2 K displays a hysteretic behavior, with $H_c = 500$ G (Figure 2). The magnetization is fully saturated at 5 T. Taking into account the cobalt content in the material (21.6%), we can calculate an average value of the magnetic moment per cobalt atom: $1.72(\pm 0.05) \mu_B/\text{Co}$, in perfect agreement with the expected bulk value.

WAXS analysis¹⁸ was performed on **1** and **2**. The radial distribution function (RDF) and the reduced intensity (Figure 3) allow for straight comparison with functions computed from four different spherical models (polytetrahedral, ϵ , hcp,

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(17) In a typical experiment, 2 mmol of DiBAH dissolved in 10 mL of toluene was added dropwise to a 10 mL toluene solution of 1 mmol of $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ at -50 °C in a vessel connected to a bubbler to allow gas evolution. The reacting medium was then allowed to come back to room temperature. The solution turns from green to black over 2 h.

(18) WAXS measurements were performed at CEMES on a dedicated two-axis diffractometer at molybdenum wavelength (0.071069 nm). Measurement time was typically 20 h per sample. Pure sample powders were sealed inside thin-walled glass capillaries 1.5 mm in diameter. Measurements were also performed on alumina powder to allow for matrix absorption and scattering corrections. Intensity was reduced by subtraction of components independent of the structure, and then Fourier transformed.

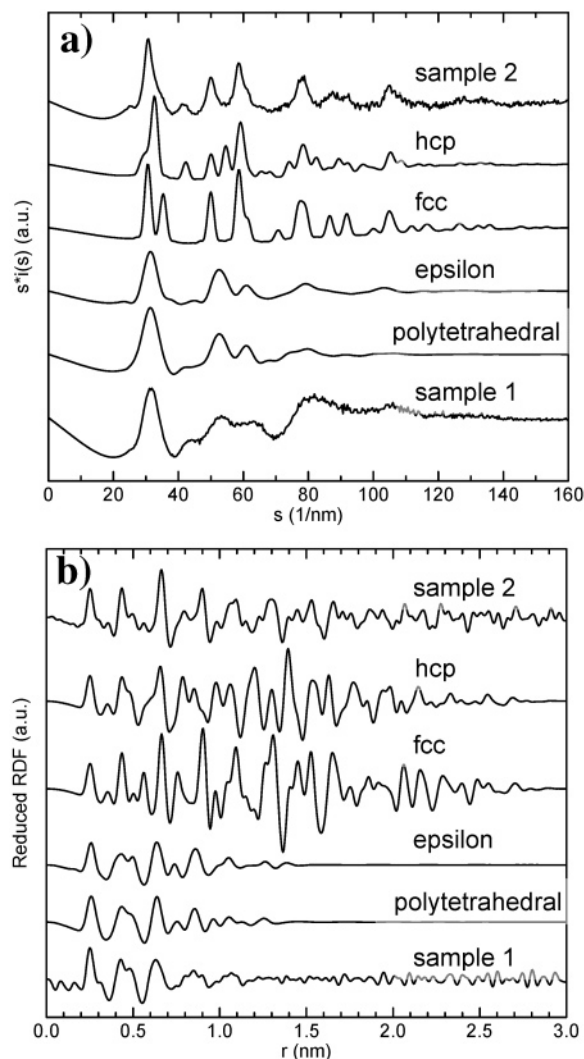


Figure 3. (a) s -weighted reduced intensity and (b) RDF of samples **1** and **2**, as computed from spherical cobalt NPs of, respectively, hcp, fcc, ϵ , and polytetrahedral structure.

and fcc) both in direct and in reciprocal space. For both samples, the first metal–metal distance, as defined by the first peak mean value, is very close to 0.251 nm like in bulk cobalt. The NPs present in **2** clearly adopt a close-packed structure. The coherence length can be estimated to 3 nm, in perfect agreement with TEM. However, a combination of fcc and hcp 3 nm large nanocrystals must be used to fit the experimental data, to obtain a good agreement in both direct and reciprocal space as shown Figure 4. This indicates either a mixture of particles with different structures or the occurrence of stacking faults. On the contrary, NPs in **1** do not adopt any of the bulk structures (hcp or fcc). The amplitude of the RDF is relatively small. The coherence length, even if difficult to accurately determine, can be evaluated to less than 1.7 nm. The distance distribution is very close to that previously observed for 1.4 nm NPs prepared from the same precursor in the presence of PVP and attributed to a polytetrahedral arrangement,¹⁹ but also to that computed from the ϵ -Co structure recently observed in NPs.^{3,20} These atomic arrangements are mostly character-

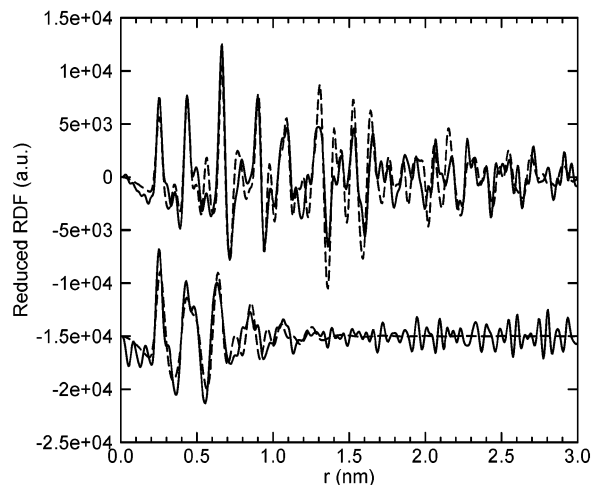


Figure 4. Reduced RDF functions of: (bottom) sample **1** (solid line), and computed function for a spherical model of polytetrahedral cobalt (dotted line); (top) sample **2** (solid line), computed function for a spherical model of hcp cobalt and fcc cobalt (dotted line). For comparison with sample **2**, functions for sample **1** are multiplied by 5.

ized by a lower local symmetry for cobalt and a reduced density as compared to the hcp and fcc structures. The coherence length is much smaller than the size observed by TEM, which evidences a highly disordered atomic arrangement in the NPs because the coherence length represents the size of the single crystalline domains. A distorted surface is not sufficient to explain such a discrepancy. It rather indicates that NPs in **1** are twinned or built from the aggregation of smaller units. Most structural features are adequately fitted using the polytetrahedral model built from connected icosahedra previously proposed¹⁹ as shown Figure 4.

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements (Co K-edge) were carried out to ascertain both the structure and the electronic state of cobalt in these samples.²¹ The results are displayed in Figure 5, as well as a reference spectrum obtained from a cobalt foil and a complementary measurement performed on **1** deliberately exposed to air. The shape of the XANES clearly evidences that particles in either sample **1** or **2** are not oxidized: neither white line nor edge shift to high energy can be observed. The RDFs, uncorrected for phase shifts, were obtained after standard analysis of EXAFS data. As compared to the reference foil, the sample **2** pattern presents a significant reduction of amplitude but remains perfectly consistent with a close-packed structure, in agreement with WAXS data. A very different pattern is observed for sample **1**: the amplitude of the peak related to the metal–metal distance is dramatically reduced, and no distance can be observed after those corresponding to the first neighbors. Furthermore, a broad peak can be observed at smaller distances, which indicates the bonding of light elements to cobalt. However, the RDF for sample **1** is

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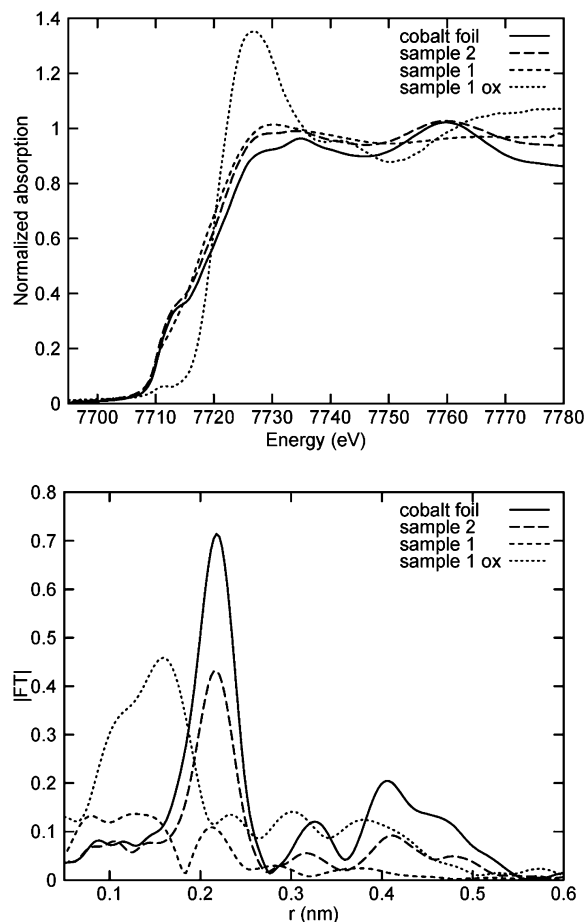


Figure 5. (top) XANES Co K-edge, (bottom) magnitude of k^2 weighted Fourier transforms uncorrected for phase shifts for sample **1** (dotted line) and sample **2** (dashed line), cobalt foil (solid line), and oxidized sample **1**, that is, sample **1ox** (small dotted line) as references.

essentially different from the pattern induced by oxidation characterized by the complete lack of the first metal–metal distance and much larger amplitude at low distances. EXAFS signal from sample **1** is actually very weak, and careful analysis is underway. However, these elements are consistent with a very large dispersion of metal–metal distances, in agreement with a model based on the association of very small units, and strong interaction between a large part of NPs atoms and light elements surface-bonded. Because distances involving light atoms connected to metallic clusters can hardly be evidenced by WAXS, this is likely to explain the discrepancy between these two complementary methods. Detailed analysis of the EXAFS spectra and comparison to models will be the subject of a forthcoming paper.²²

We are thus in the presence of two assemblies of NPs of roughly the same size but displaying very different magnetic and structural properties. This has to be related to the difference in chemical surrounding of the particle surface.

Let us discuss first the magnetic properties of these NPs. The most striking result is the high differential susceptibility observed in high fields and leading to a very low magnetization at 5 T in sample **1**. The fact that the NPs adopt a structure very different from the bulk one, even if it may lead to strong changes in magnetic anisotropy, should not

be responsible for this strong decrease in magnetization. Indeed, bcc, fcc, and hcp phases present very close values of magnetic moment per atom (1.6–1.7 μ_B/Co). It is also the case in ϵ -Co, where the value determined is close to 1.7 μ_B/Co , or in polytetrahedral arrangements, where no magnetization reduction could be evidenced, whereas the atom packing is very different from the bulk one.^{3,12} This magnetization damping could then either arise from partial oxidation of the NPs surface or be attributed to a strong damping of the magnetic moment of the surface atoms upon coordination of the ligands or other chemical species at their surface. A strong coordination effect would also be in agreement with the fact that the magnetization is difficult to saturate, either through a strong alteration of surface anisotropy or via the formation of a diamagnetic surface layer. Oxidation can be ruled out given the XANES and EXAFS spectra. This sample was synthesized under a di-hydrogen pressure, whereas sample **2** was not. Actually, surface hydrides are expected to be present at the surface of the particles as recently demonstrated for Ru NPs.²³ One can thus question the effect of hydrogen adsorption on the magnetic properties. However, previous experiments have shown that hydrogen adsorption induces only a small decrease of magnetization in the case of cobalt.⁵ Moreover, we have demonstrated that NPs prepared in the same conditions of hydrogen pressure, but stabilized by poly(vinylpyrrolidone), displayed magnetic properties similar to those of free-standing Co NPs,¹² thus ruling out the possible role of coordinated hydrides in the low Ms value found for sample **1**. However, the ligand used during the synthesis of **1** can strongly interact with hydrides coordinated to transition metals.²⁴ In this particular case, the formation of hydrido aluminate species at the NPs surface should occur, which could then transform into tricoordinated surface alkyl aluminum species as depicted in Figure 2, inset a.^{25–28} Given the large excess of DiBAH used during the synthesis and the alkylating properties of this aluminum compound, formation of surface alkyl radicals may also be envisaged, in agreement with the short distance observed by EXAFS. The surface of the NPs could then be regarded as electronically depleted. It is well known that electron-withdrawing ligands such as carbon monoxide deprive the surface atoms from their magnetic properties.²⁹ We assume that a similar phenomenon takes place in sample **1** and accounts for the observed low magnetization.

In comparison, NPs in **2** display unaltered magnetic properties. This is a strong indication that the stabilizing ligand is of a different chemical nature and most probably

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that the strongly donating amido group participates in the stabilization of the NPs. Thus, σ -donating ligands such as amines have proven not to be detrimental to the magnetic properties of cobalt³⁰ and nickel NPs.^{31,32} The driving force of the reaction between the cobalt complex $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$ and DiBAH is most probably the initial formation of very stable Al–N bonds as observed in lanthanide chemistry.³³ This would lead to a transient Co hydride species, which would then rapidly decompose into cobalt atoms and the amine, $\text{HN}(\text{SiMe}_3)_2$. So we suggest that the particles surface may be covered by amines and/or amido aluminum species that are either monomeric, such as depicted in Figure 2 (inset b), or possibly polymeric.

The observed difference in structure can also be related to the different binding behaviors of the ligands. NPs with a structure similar to **1** have previously been obtained through hydrogenation of $\text{Co}(\eta^3\text{C}_8\text{H}_{13})(\eta^4\text{C}_8\text{H}_{12})$ in the presence of poly(vinylpyrrolidone), with, however, small mean diameters (1.4 nm).¹⁹ A comprehensive study of their magnetic properties has shown that they were similar to those expected for free-standing cobalt NPs,¹² that is, that the polymer matrix has few or no interactions with the NPs, leading to surface metal atoms undercoordinated and electronically unsaturated. It is noteworthy that the formation of ϵ -cobalt has been reported to be promoted by a careful choice of the ligands used during the synthesis.^{3,20} Hence, in the presence of TOPO or PR_3 ligands, which are known to damp the magnetic properties of NPs, cobalt NPs adopt the ϵ -cobalt structure, whereas a fcc structure is observed in the absence of such ligands.³⁴ In sample **1**, the electron deficiency is also important. On the contrary, NPs in sample **2**, the surface of

which is surrounded by donating ligands, adopt a compact structure displaying features of both fcc and hcp phases. It is noteworthy that the hcp structure is not often reported for such small sizes, especially for NPs obtained at low temperature. It is suggested that coordination of a σ -donor ligand at their surface could favor this structure.

The difference in structure could also be related to the synthesis conditions. However, **1** is obtained at room temperature by a slow reaction process (48 h), whereas the formation of **2** is fast at -50 °C. This is in contradiction with the expected kinetic quenching of a metastable structure and further attests the influence of the coordinated ligand on the structure adopted by the NPs.

In conclusion, the two syntheses reported therein show that an electron-withdrawing stabilizing shell (alkyl aluminum species) promotes lower symmetry and packing density in Co NPs as well as a decrease in magnetization, whereas a compact structure and bulk magnetization are obtained for NPs, the surface of which is electronically enriched (via coordination of amido aluminum species or amine). This emphasizes the major role played by chemistry in the control of both magnetic and structural features at the nanometer scale.

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