Keywords: bioaffinity studies · combinatorial chemistry · molecular recognition · NMR spectroscopy

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A Solution-Phase Chemical Approach to a New Crystal Structure of Cobalt**

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Cobalt has long been known to have two crystal structures—close-packed hexagonal (hcp) and face-centered cubic (fcc). While both phases can coexist at room temperature, the fcc structure is thermodynamically preferred above 450 °C and the hcp phase is favored at lower temperatures.[1] For small particles, however, the fcc structure appears to be preferred even below room temperature.[2] The existence of fcc and hcp cobalt was first reported by Hull[3] in 1921 after analyzing diffraction patterns of metallic powders prepared by several methods. Krainer and Robitsch[4] reported observing new diffraction lines in samples prepared by spark erosion of bulk cobalt surfaces, but the structure was never fully established. Kajiwara et al.[5] observed several new lines in the diffraction pattern of cobalt nanoclusters prepared by plasma evaporation and the subsequent condensation of the metal, but attributed these lines to a form polymorphous to the two known structures. Similar results are reported by Leslie-Pelecky et al.[6] with cobalt particles prepared by the reduction of cobalt salt in solution with metallic lithium. A recent report by Respaud et al.[7] provides some evidence for a new structure of cobalt present in small cobalt clusters produced by the decomposition of organometallic precursors, but the structure was not identified. Herein we report and identify a new stable structure for elemental cobalt.

The fcc and hcp phases of cobalt are close-packed structures that differ only in the stacking sequence of atomic planes in the 111 direction. Low activation energy for formation of stacking faults often leads to the formation of both phases in the same sample under high-temperature crystallization techniques, such as melting–crystallization and evaporation–condensation. Low-temperature solution chemistry methods, on the other hand, often yield exclusively one phase of cobalt.

We used thermal decomposition of octacarbonyldicobalt in solution in the presence of trioctylphosphane oxide (TOPO) as a coordinating ligand to prepare cobalt nanoclusters. This method provides a "clean" route for the preparation of the material since elemental cobalt is the only nonvolatile product of the reaction: $[Co_2(CO)_8] \rightarrow 2\,Co + 8\,CO$. The resulting powder was highly susceptible to magnetic fields generated by a small permanent magnet, suggesting that it consisted of metallic cobalt. Transmission electron microscopy (TEM) showed that the powder consisted of roughly spherical

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particles with an average diameter of 20 nm and a 15% size distribution. Later experiments showed that the size of the crystals is not limited to this range. In fact, injection at higher temperature yields regular polyhedron-shaped faceted crystals as large as 0.3 μm and possibly even larger (Figure 1). Elemental analysis gave the following atomic percentage: Co 83%, O 11%, other elements (C, H) 6%. The presence of oxygen indicates surface oxidation of the cobalt particles, corresponding to a coverage of one to two monolayers of cobalt oxide for particle sizes in the 20 nm range. The other elements, we believe, come from residual organic solvents adsorbed on the particle surfaces. The absence of phosphorus in the elemental analysis indicates that TOPO was completely removed during washing of the particles. It should be emphasized here that freshly synthesized cobalt nanoparticles are extremely reactive towards oxidation. In fact, rapid exposure to air results in immediate oxidation accompanied by a red glow. Therefore, even simply washing the particles in organic solvents inevitably leads to surface oxidation by residual moisture and dissolved air. The resulting oxide layer appears to passivate the surface of the particles and considerably reduce the speed of further oxidation.

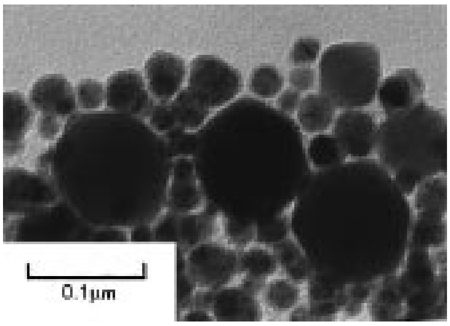

Figure 1. TEM image of cobalt crystals with the new ε-cobalt structure.

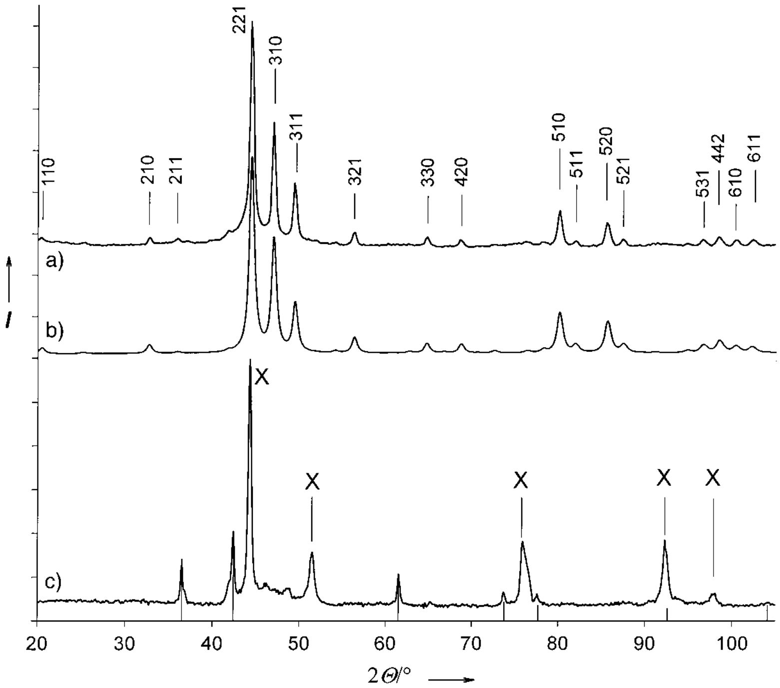

Figure 2. X-ray powder diffraction pattern of the ε-cobalt structure: a) experimental; b) calculated; c) the sample shown in a) after being heated to 500 °C, peaks corresponding to fcc cobalt are denoted by X, peaks corresponding to CoO are marked with a stick spectrum.

Table 1. Fractional atomic coordinates in the unit cell of ε-cobalt structure.[a]

	x	*y*	*z*
Type I			
1	*v*	*v*	*v*
2	*v* + ½	½ − *v*	1 − *v*
3	1 − *v*	*v* + ½	½ − *v*
4	½ − *v*	1 − *v*	*v* + ½
5	¾ − *v*	¾ − *v*	¾ − *v*
6	*v* + ¼	¼ − *v*	*v* + ¾
7	¼ − *v*	*v* + ¾	*v* + ¼
8	*v* + ¾	*v* + ¼	¼ − *v*
Type II			
9	1 − *u*	*u* + ¾	⅜
10	½ − *u*	¾ − *u*	⅝
11	*u*	*u* + ¼	⅛
12	*u* + ½	¼ − *u*	⅞
13	⅜	1 − *u*	*u* + ¾
14	⅝	½ − *u*	¾ − *u*
15	⅛	*u*	*u* + ¼
16	⅞	*u* + ½	¼ − *u*
17	*u* + ¾	⅜	1 − *u*
18	¾ − *u*	⅝	½ − *u*
19	*u* + ¼	⅛	*u*
20	¼ − *u*	⅞	*u* + ½

[a] $u = 0.20224$, $v = 0.06361$.[9]

Figure 2a shows an X-ray powder diffraction pattern of the reaction product.[8] This pattern does not correspond to either of the two known structures of cobalt. In fact, neither the positions of the peaks nor their intensity distribution correspond to known cobalt phases. After detailed analysis it was concluded that this pattern corresponds to a new, previously unknown phase of cobalt, which we call ε-cobalt. This structure is cubic (space group $P4_132$) with a unit cell parameter $a = 6.097 \pm 0.001$ Å. The unit cell structure is similar to that of β-manganese (a high-temperature phase of manganese).[9] It contains 20 cobalt atoms, which are divided into two types: twelve atoms of Type I and eight atoms of Type II (Table 1). These two types of atoms differ in their local coordination. Unlike an ideal close-packed structure, which has twelve nearest neighbors, ε-cobalt has only three nearest neighbors for Type I and two nearest neighbors for Type II atoms (Table 2). This results in a structure for ε-cobalt that is less dense than both the hcp and fcc structures. The calculated density of ε-cobalt is 8.635 $\mathrm{g\,cm^{-3}}$, compared to 8.788 $\mathrm{g\,cm^{-3}}$ and 8.836 $\mathrm{g\,cm^{-3}}$ for the fcc and hcp structures, respectively.[1] The calculated diffraction pattern for the new phase (Figure 2b) is in excellent agreement with experimental data.[10] The comparison shows that the experimental pattern is clean and corresponds to a pure ε-cobalt structure. The position and intensity of each peak is precisely reproduced and there are no peaks corresponding to either known cobalt phases or cobalt oxide. Numerical values for experimental and calculated peak positions and intensities are shown in Table 3. A model unit cell for ε-cobalt is shown in Figure 3.

Table 2. Local coordination for the two types of Co atoms in ε-cobalt.

Near neighbor type (number)	Interatomic distance [Å]	Near neighbor type (number)	Interatomic distance [Å]
Type I		Type II	
Type I (3)	2.281(9)	Type I (2)	2.487(2)
Type II (3)	2.487(2)	Type I (2)	2.543(4)
Type II (3)	2.543(4)	Type I (2)	2.587(0)
Type II (3)	2.587(0)	Type II (4)	2.554(6)
Type II (2)	2.580(1)		

Table 3. Assignments of reflections and comparison between observed and calculated values for ε-cobalt.

$2\theta_{obs}$	Obs. intensity	*hkl*	Cell parameter [Å][a]	$2\theta_{calc}$	Calcd intensity
32.83	3.3	210	6.1002	32.848	4.5
36.10	0.6	211	6.0946	36.085	0.8
44.57	100	221	6.0989	44.585	100
47.14	55	310	6.0968	47.138	58
49.59	27	311	6.0970	49.590	25
64.88	4	330	6.0975	64.886	5
80.30	22	510	6.0966	80.293	21
82.15	3	511	6.0968	82.147	4
85.84	18	520	6.0966	85.832	19
96.85	4	531	6.0968	96.845	5
98.67	8	442	6.0981	98.694	8
100.52	6	610	6.0984	100.544	4.5
102.40	5	611	6.0980	102.422	4

[a] Average = 6.097 ± 0.001.

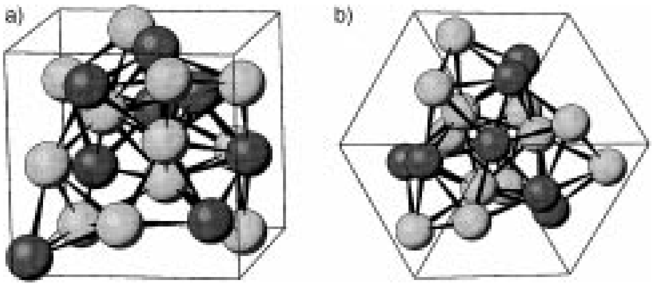

Figure 3. The unit cell of ε-cobalt: a) unit cell cube filled with eight atoms of Type I (dark) and twelve atoms of Type II (light); b) 111-projection of the same cube showing threefold symmetry along its main diagonal.

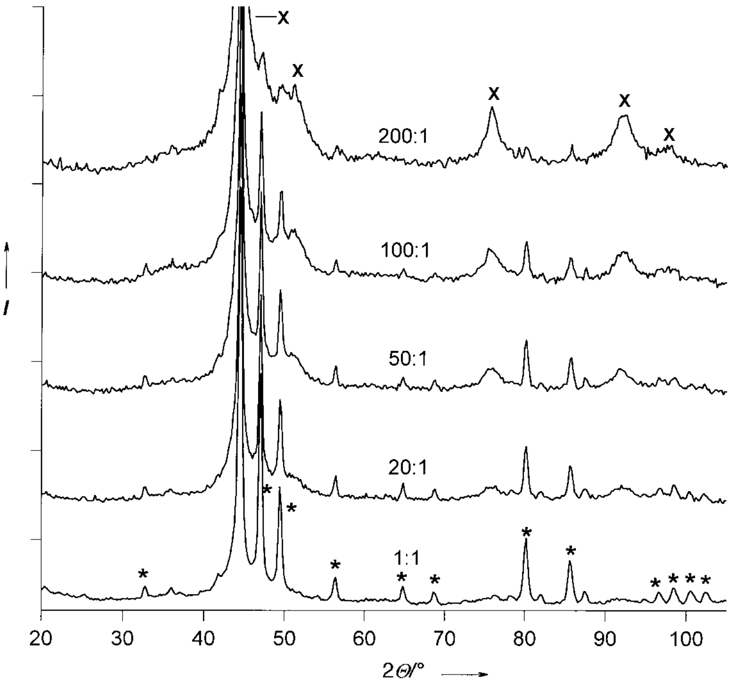

Figure 4. Evolution of the X-ray diffraction pattern of cobalt nanocrystals prepared with different concentrations of TOPO. The numbers shown correspond to the ratio of cobalt atoms to TOPO molecules in the reaction mixture. The gradual change from fcc (peaks denoted by X) to ε-cobalt (selected peaks denoted by *) with increasing concentration of TOPO is clearly observed. Sharpening of the peaks corresponding to improved crystallinity of the nanocrystals is also observed.

The magnetic moment per atom in ε-cobalt, measured as 1.70 μ_B, is similar, within our experimental error, to that of the two known structures (1.75 μ_B and 1.72 μ_B for bulk fcc and hcp cobalt).[11]

The new ε-cobalt phase appears to be metastable under normal conditions. Although stable at room temperature for at least several months, heating the sample shown in Figure 2a to 500 °C completely transforms it to the known fcc phase (Figure 2c).[12] Subsequent cooling does not return the sample to its original ε-cobalt structure. The same preparation method but without the presence of TOPO yields nanocrystals with a pure fcc phase. When TOPO is added, ε-cobalt is formed along with fcc cobalt. Increasing the concentration of TOPO in the reaction mixture leads to the exclusive formation of ε-cobalt (Figure 4). Tight coordination of ligand molecules (TOPO) around the growing crystal and around solubilized cobalt atoms is responsible for changing the energetics of growth in favor of the new, less dense phase. In fact, the particular synthesis of this paper is not unique in producing ε-cobalt. Sun and Murray[13] have recently confirmed our assignment of the structure of ε-cobalt in nanocrystals obtained by reducing cobalt salts in solution in the presence of alkylphosphanes as the coordinating ligands. Due to its metastability, ε-cobalt may only be accessible by solution-phase approaches, rather than more common techniques, such as varying temperature and pressure.

The discovery of a new phase for a common element is an example of the critical role that ligands and surfactants can play in determining the resulting structure of crystals grown in solution at low temperatures. Such solution-phase reactions are often controlled kinetically rather than thermodynamically, leading to the initial trapping and growth of metastable phases. Similar low-temperature growth conditions may lead to the discovery of previously unknown structures for other elements and for more complex systems. There is a strong correlation between crystal structure and the magnetic properties of cobalt. The anisotropic high magnetic coercivity hcp phase is the preferred structure for permanent magnet applications (recording media, etc), while the more symmetric low coercivity fcc phase is useful for soft magnetic applications. The newly discovered structure of cobalt may display magnetic properties different from the two previously known structures, and this could be scientifically interesting and technologically useful.

Experimental Section

$[Co_2(CO)_8]$ (2.5 g, Strem Chemicals, Inc.) was dissolved in dry toluene (30 mL) under air-free conditions, filtered, and then loaded into a syringe. Trioctylphosphane oxide (TOPO, 5 g, Strem Chemicals, Inc.) was placed in a 100 mL flask and dried under vacuum at 150 °C. The temperature was then brought down to 50 °C, and the solution of $[Co_2(CO)_8]$ was quickly injected into the flask while vigorously stirring under a nitrogen atmosphere. The temperature was slowly increased to 110 °C. This was accompanied by evolution of carbon monoxide and by a color change of the reaction mixture from deep blue to black. After completion of the reaction the heating mantle was removed, and the mixture was allowed to cool to room temperature. The product of the reaction was isolated as a black powder and was thoroughly washed with hexane and methanol and dried under nitrogen.

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A Triphenylamine Derivative with Three *p*-(*N*-*tert*-Butyl-*N*-oxylamino)phenyl Radical Units and Yet a Doublet Ground State**

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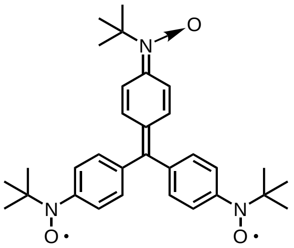
Intramolecular ferromagnetic interactions of electron spins in polyradicals are of current interest in the design of molecular ferromagnets.[1] Previously, we reported that the oxidation of tris[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]methane with silver(I) oxide gave the quinonoid diradical **1**, which has a robust triplet ground state.[2] When the methane carbon atom in **1** is replaced with a nitrogen atom to make tris[*p*-(*N*-*tert*-butyl-*N*-oxylamino)phenyl]amine (**2**), a quinonoid structurerequires a zwitterionic structure. Hückel MO calculations show that tris(*p*-methylenephenylene)methane, a simplified model of **1**, has two degenerate SOMOs similar to those of trimethylenemethane (TMM).[3] Since the corresponding amine has one more π electron than the methane, the former is expected to become isoelectronic with the anion radical of the latter and therefore exist as a doublet monoradical. We report here the synthesis, structure, and magnetic properties of **2**.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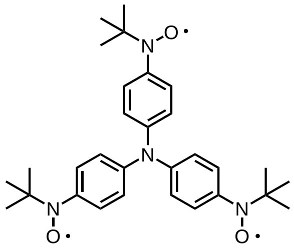
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Triradical **2** was obtained by oxidation of tris[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]amine with Ag_2O. A single crystal for an X-ray diffraction measurement was obtained by slow evaporation of a solution of **2** in *n*-heptane/dichloromethane.[4] The molecule has no threefold axis passing through the central nitrogen atom (Figure 1). The *p*-phenylene rings are tilted by 29.8°, 34.3°, and 57.3° from the plane formed by C1, C11, and C21. The intramolecular distances between the oxygen atoms of the oxylamino groups are 9.73

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