Thermal decomposition of \([\text{Co}(\text{en})_3][\text{Fe(CN)}_6] \cdot 2\text{H}_2\text{O}\): Topotactic dehydration process, valence and spin exchange mechanism elucidation

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**Abstract**

**Background:** The Prussian blue analogues represent well-known and extensively studied group of coordination species which has many remarkable applications due to their ion-exchange, electron transfer or magnetic properties. Among them, Co-Fe Prussian blue analogues have been extensively studied due to the photoinduced magnetization. Surprisingly, their suitability as precursors for solid-state synthesis of magnetic nanoparticles is almost unexplored.

In this paper, the mechanism of thermal decomposition of \([\text{Co}(\text{en})_3][\text{Fe(CN)}_6] \cdot 2\text{H}_2\text{O}\) (1a) is elucidated, including the topotactic dehydration, valence and spins exchange mechanisms suggestion and the formation of a mixture of \(\text{CoFe}_2\text{O}_4 - \text{Co}_3\text{O}_4\) (3:1) as final products of thermal degradation.

**Results:** The course of thermal decomposition of 1a in air atmosphere up to 600°C was monitored by TG/DSC techniques, \(^{57}\text{Fe}\) Mössbauer and IR spectroscopy. As first, the topotactic dehydration of 1a to the hemihydrate \([\text{Co}(\text{en})_3][\text{Fe(CN)}_6] \cdot 1/2\text{H}_2\text{O}\) (1b) occurred with preserving the single-crystal character as was confirmed by the X-ray diffraction analysis. The consequent thermal decomposition proceeded in further four stages including intermediates varying in valence and spin states of both transition metal ions in their structures, i.e. \([\text{Fe}^{II}\text{(en)}_2(\mu-\text{NC})\text{Co}^{III}\text{(CN)}_4], \text{Fe}^{III}\text{(NH}_2\text{CH}_2\text{CH}_3)_2(\mu-\text{NC})\text{Co}^{III}\text{(CN)}_3]\) and \([\text{Fe}^{III}\text{Co}^{II}\text{(CN)}_5]\), which were suggested mainly from \(^{57}\text{Fe}\) Mössbauer, IR spectral and elemental analyses data. Thermal decomposition was completed at 400°C when superparamagnetic phases of \(\text{CoFe}_2\text{O}_4\) and \(\text{Co}_3\text{O}_4\) in the molar ratio of 3:1 were formed. During further temperature increase (450 and 600°C), the ongoing crystallization process gave a new ferromagnetic phase attributed to the \(\text{CoFe}_2\text{O}_4 - \text{Co}_3\text{O}_4\) nanocomposite particles. Their formation was confirmed by XRD and TEM analyses. In-field (5 K / 5 T) Mössbauer spectrum revealed canting of Fe(III) spin in almost fully inverse spinel structure of \(\text{CoFe}_2\text{O}_4\).

**Conclusions:** It has been found that the thermal decomposition of \([\text{Co}(\text{en})_3][\text{Fe(CN)}_6] \cdot 2\text{H}_2\text{O}\) in air atmosphere is a gradual multiple process accompanied by the formation of intermediates with different composition, stereochemistry, oxidation as well as spin states of both the central transition metals. The decomposition is finished above 400°C and the ongoing heating to 600°C results in the formation of \(\text{CoFe}_2\text{O}_4 - \text{Co}_3\text{O}_4\) nanocomposite particles as the final decomposition product.

**Keywords:** Hexacyanidoferrate, Crystal structure, Thermal behavior, Mössbauer spectroscopy, Topotactic dehydration, Nanocomposite particles, \(\text{CoFe}_2\text{O}_4\)

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Background

Transition metal hexacyanido complexes represent an enormous and well-known group of coordination species. The Prussian blue, with the idealized formula $\text{Fe}_4[\text{Fe(CN)}_6]_3\cdot n\text{H}_2\text{O}$, is one of the oldest examples of a hexacyanido complex combining interesting structural features and magnetic properties. Therefore, many Prussian blue analogues [1], e.g. $\text{M}_x\text{A}[\text{B(CN)}_6]_n\cdot n\text{H}_2\text{O}$ (M is alkali metal, A and B are different divalent/trivalent transition metals, $x \leq 1$, $z \leq 1$, if $z < 1$ B-sites are fractionally occupied and B-vacancies are present) have been extensively studied due to their sorption, ion-exchange, electron transfer or magnetic properties, and in recent years, many applications using PBAs usually in form of thin films or nanoparticles have been developed [2,3].

The reversible intercalation of alkali metal cations due to the zeolite-like structure of PBAs [4] has been employed in still active development of the selective adsorbent of $^{137}\text{Cs}$ from radioactive waste waters [5] or more recently, in construction of a new active electrode material for Li-ion batteries ($\text{A}_x\text{M}_n[\text{Fe(CN)}_6]_y$ where $\text{A} = \text{K, Rb}$, $x < 1$, $1 < y < 1.5$) [6]. The electrochemical coating of electrodes with thin film of PBAs or deposition with coordinated PBAs nanoparticles [2,7,8] gave rise to a large number of amperometric and potentiometric sensors for non-electroactive ions or $\text{H}_2\text{O}_2$ [3,9], electrochromic sensors [10] or biosensors [11]. The electrochromic or thermochromic behavior of electrochemically prepared PBAs thin films was further applied in the construction of different devices including electrochromic displays and pattering devices, thermal probes or photoelectrochemical/photocatalytical solar energy converters [12].

PBAs also represent an enormous and important group of molecular magnets [1,13-15] which play important roles in many applications mainly in molecular electronics and magnetic/electronic devices [16,17]. During the experimental race to enhance the Curie temperatures of molecular magnets based on PBAs, the systems incorporating V(II) gave the most promising results and $\text{KV}[\text{Cr(CN)}_6]_2\cdot 2\text{H}_2\text{O}$ was found to possess the highest $T_c$ even above the boiling point of water (376 K) [18]. This invention of room temperature molecule-based magnets opens interesting applications as magnetic switches, oscillators or magnopto-optical data storage devices. The cyanido-bridged networks, serving as a platform for the preparation of coordination nanoparticles based on Prussian blue, has also been employed for the controlling/tuning of magnetism by temperature (e.g. $\text{A}_3[\text{M}^{II}\text{M}^{III}][\text{CN}]_6$), $\text{A} =$ alkali metal ion) [2] or light irradiation (with a general formula of $\text{A}_x\text{Co}_y[\text{Fe(CN)}_6]_z\cdot n\text{H}_2\text{O}; x, y, z$ are independent) [8].

An important feature of especially Co-Fe Prussian blue systems is the phenomenon of photoinduced magnetization or photoreversible enhancement of magnetization [19-21] which has been observed in e.g. $\text{Rb}_{1.8}\text{Co}^{III}_0\text{Co}^{II}_3\cdot 13\text{H}_2\text{O}$ [22,23], $\text{Nd}_{0.3}\text{Co}_{1.33}\text{Fe(CN)}_6\cdot 4.5\text{H}_2\text{O}$ [19], or $K_{0.4}\text{Co}_{1.4}\text{Fe(CN)}_6\cdot 5\text{H}_2\text{O}$ [20]. These compounds are efficient 3D-ferrimagnets at low temperatures ($T_c < 30$ K) due to the presence of majority of Fe$^{III}$–Co$^{II}$ diamagnetic pairs which undergo upon irradiation photoinduced electron transfer resulting in paramagnetic Fe$^{III}$–Co$^{II}$ species. Such transformation is accompanied by elongation of the Co–N bond lengths (0.15–0.20 Å) which is possible only in the case of flexible inorganic network provided by the existence of hexacyanidoferrate vacancies occupied by water molecules.

Transition metal hexacyanido complexes have been also successfully utilized as building blocks for constructing oligo- and polynuclear assemblies derived from the Prussian blue and a large number of such organic–inorganic hybrid materials containing various organic ligands, mainly N-donor linear or macrocyclic ligands, have been extensively studied [24-28]. These compounds were also found to behave as molecular magnets [29] with potential applications as molecular devices or memory devices. Some of them also revealed very specific optical properties including ion pair charge-transfer (IPCT) [30] transitions corresponding to the transfer of electrons from the complex anions to the complex cations in the visible and near-ultraviolet spectral regions. This phenomenon was confirmed for ion pair compounds involving both $[\text{Co(en)}_3]^{3+}$ and $[\text{M(CN)}_4]^{3+}$ (for $x = 6$, $M = \text{Fe, Ru, Os}$; for $x = 8$, $M = \text{Mo, W}$) complex ions [31]. An irradiation of solutions containing these species into the IPCT absorption band ($\lambda_{\text{irr}} = 405$ or 510 nm) leads to a structure re-arrangement and the formation of bi- or trinuclear species. For the iononic pairs $[\text{M(NH}_3)_2\text{L}]^{3+}$ and $[\text{Fe(CN)}_6]^{3-}$ (M = Ru, Os; L = $\text{NH}_3$ or $\text{H}_2\text{O}$), an inverse direction of the electron transfer of the IPCT transition (from the cation to the anion) was found [32].

Only ten X-ray structures of discrete dinuclear Co–Fe cyanido-bridged complexes have been reported up to now, whereas about ninety hits corresponding to poly- or oligomeric Co–Fe cyanido-bridged complexes have been deposited within the Cambridge Structural Database up to now [33]. Most of the dinuclear complexes have the general formula of $[L_n\text{Co}^{III}_n\text{–NC}–\text{Fe}^{II}(\text{CN})_6]^{1-}$, where $L_n$ stands for a macrocyclic ligand, and they have been systematically studied by Bernhardt et al. [34-36]. Up to date, similar number of ionic pair Co(III)-Fe(II) complexes have been structurally characterized. They always contain hexacyanidoferrate(III) anion and Co(III) complexed by ammonia [37], $\text{en}$ [38-41], $\text{bipy}$ [42-45], $\text{terpy}$ [46], or other suitable ligands [47]. Despite Co(III)-Fe(III) hexacyanidoferrates represent very important group of compounds bearing a broad spectrum of important physico-chemical properties, surprisingly only a little...
attention has been paid to the monitoring of the thermal behavior of these compounds [48,49]. Especially the fact that they can serve as suitable precursors for thermally induced solid-state synthesis of magnetic nanoparticles [50,51] is almost unexplored.

The dehydration process of the monohydrate [Co(en)$_3$]$\cdot$H$_2$O was previously described in details by our working group [40] and recently, thermal decomposition of [Co(en)$_3$]$\cdot$3[Co(CN)$_6$]$\cdot$2H$_2$O in different atmospheres has been published as well [52]. In the present work, we also report the thermal degradation of [Co(en)$_3$]$\cdot$[Fe(CN)$_6$]$\cdot$2H$_2$O (1a) which was obtained upon recrystallization from water at 60°C. But furthermore, we concentrate on the progress of thermal decomposition of [Co(en)$_3$]$\cdot$[Fe(CN)$_6$]$\cdot$2H$_2$O under dynamic heating in air which includes the topotactic dehydration process of [Co(en)$_3$]$\cdot$3[Co(CN)$_6$]$\cdot$2H$_2$O in different atmospheres which has been published as well [52]. In the present work, we also report the thermal degradation of [Co(en)$_3$]$\cdot$[Fe(CN)$_6$]$\cdot$2H$_2$O (1a) which was obtained upon recrystallization from water at 60°C. But furthermore, we concentrate on the progress of thermal decomposition of [Co(en)$_3$]$\cdot$[Fe(CN)$_6$]$\cdot$2H$_2$O under dynamic heating in air which includes the topotactic dehydration process of the starting complex and gradual ligand liberation/decomposition resulting in the formation of CoFe$_2$O$_4$-Co$_3$O$_4$ nanocomposite particles as a final product of the thermal conversion. Based on the elemental and TG/DSC analyses, IR and $^{57}$Fe Mössbauer spectra, we suggest and discuss the unique decomposition mechanism accompanied by changes in the valence and spin states of both transition metal ions.

**Results and discussion**

**Synthesis, X-ray structure and spectral characterization of [Co(en)$_3$]$\cdot$[Fe(CN)$_6$]$\cdot$2H$_2$O (1a)**

In contrast to our previous study which described a topotactic dehydration process of [Co(en)$_3$]$\cdot$[Fe(CN)$_6$]$\cdot$H$_2$O into [Co(en)$_3$]$\cdot$[Fe(CN)$_6$] by means of single crystal X-ray analysis and Mössbauer spectroscopy [40], herein, we strive to elucidate the mechanism of the thermal decomposition of [Co(en)$_3$]$\cdot$[Fe(CN)$_6$]$\cdot$2H$_2$O based on a complete characterization of the decomposition intermediates. The ionic pair [Co(en)$_3$]$\cdot$[Fe(CN)$_6$]$\cdot$2H$_2$O complex was prepared by the straightforward reaction between [Co(en)$_3$]$^{3+}$ and [Fe(CN)$_6$]$^{3-}$, used as building blocks, in DMF [38]. The efforts to prepare the title compound by an one-pot redox reaction in water using CoCl$_2$$\cdot$6H$_2$O instead of [Co(en)$_3$]$\cdot$Cl$_3$ were unsuccessful probably due to the incomplete coordination of en and formation of Co(II)-involving PBA [23]. The synthesis following the Bok's published procedure led to the formation of the dihydrated complex, however, two products, i.e. the dihydrated and monohydrated complexes, can be obtained after the product recrystallization from hot water in dependence on the rate of cooling of the solution. Concretely, the monohydrate is formed in the case of fast cooling of the solution heated up to 90°C, while the dihydrate is formed in the case of slow cooling of the 60°C warm solution.

As first, the molecular and crystal structures of 1a have been determined by using single crystal X-ray analysis (Figure 1, Table 1). The crystallographically independent part of the molecule consists of the [Co(en)$_3$]$^{3+}$ cation, two halves of the [Fe(CN)$_6$]$^{3-}$ moiety with the iron(III) atoms lying on special positions (inversion centers) and two crystal water molecules (Figure 1). As the structure possesses an inversion center, both $\Delta\delta\delta\delta$ (let$_3$) and $\Lambda\Lambda\Lambda\Lambda$ (ab$_3$) conformations of the [Co(en)$_3$]$^{3+}$ cations are present [54]. The Co(III) atom is coordinated by six nitrogen atoms from three chelating molecules of en in a distorted octahedral geometry. The Co–N bond lengths range from 1.955(2) to 1.981(2) Å (Table 2), and surprisingly, these values are significantly shorter than those determined for the same structure by Bok [1.996(3)–2.035(4) Å] [38]. For comparison, very similar values were found for [Co(en)$_3$I$_3$$\cdot$H$_2$O (1.950(4)–1.981(4) Å) [55] and for [Co(en)$_3$]Cl$_3$ (1.967(11) Å) [56], while they are much more distributed in [Co(en)$_3$]Cl$_3$$\cdot$FeCl$_3$$\cdot$Cl$_2$$\cdot$H$_2$O (1.919(5)–2.002(5) Å) [57]. The differences may be caused by the counter-ion that significantly influences non-bonding interactions within the crystal structure and thus, a distortion in the vicinity of the central Co(III) atom can be found as a consequence of these interactions.

In the crystal structure, the Fe(III) atoms are coordinated by six carbon atoms originating from terminal cyanide groups. While the [FeCl$_4$] octahedron is almost regular (the Fe–C distances range from 1.944(3) to 1.951(3) Å), the [FeCl$_4$] octahedron is slightly compressed with the shorter axial Fe1A–C2A distances (1.932(3) Å) as compared to the equatorial ones (1.941(3) and 1.946(3) Å) (Table 2). Such type of deformation of the hexacyanoferrate(III) anions was already observed, e.g. in [FeCl$_4$]$_3$·6H$_2$O, where the Fe–C bond lengths range from 1.931(4) to 1.953(4) Å [58]. The remaining geometric parameters determined for [Fe(CN)$_6$]$^{3-}$ in 1a are comparable to those found for the same complex anions in other compounds, e.g. in [Ni(tren)$_2$]$\cdot$[Fe(CN)$_6$]$\cdot$6H$_2$O [59] or [Ni(en)$_2$]$\cdot$[Fe(CN)$_6$]$\cdot$2$\cdot$2H$_2$O [60].

The secondary structure of 1a is further stabilized by the O–H⋯O, O–H⋯N and N–H⋯N hydrogen bonds together with the C–H⋯N and N–H⋯C non-covalent contacts connecting the complex ions and crystal water molecules (Figure 2, Table 3).

The information on the local electronic state of the iron atom can be quantitatively obtained from $^{57}$Fe Mössbauer spectra. Concretely, the isomer shift, $\delta$, which is related to the s-electron density at the nucleus and quadrupole splitting, $\Delta$, related to the electric field gradient, are crucial parameters sensitive to the oxidation and spin states of iron atom as well as its coordination number. Thus, room temperature Mössbauer spectrum of 1a confirmed the presence of Fe(III) ions in low-spin state because it consists a symmetrical doublet.
with isomer shift $\delta = -0.17$ mm/s and quadrupole splitting $\Delta E_Q = 0.85$ mm/s (Figure 3). The values of these parameters are typical for the hexacyanidotris(III) anion [61]. In measured IR spectra, typical sharp and strong absorption bands at 2117 and 2107 cm$^{-1}$ corresponding to the $\nu$(C≡N) stretching vibration were identified (Figure 4). They well document the presence of terminal coordinated cyanide groups because the vibration frequency of free CN$^-$ anion (about 2080 cm$^{-1}$) is blue shifted due to a coordination (removing electrons from weakly antibonding $\sigma$ orbital during metal-carbon $\sigma$ bond formation) like in K$_3$[Fe(CN)$_6$] which displays one sharp absorption band at 2118 cm$^{-1}$ [41,62]. In comparison with K$_3$[Fe(CN)$_6$], there is a splitting of the absorption band that can be explained by lowering of the $O_h$ site symmetry of the hexacyanidoferrate (III) anion. Otherwise, broad absorption bands due to the O–H (~3380 cm$^{-1}$), N–H (~3234 cm$^{-1}$) or C–H (~3095 cm$^{-1}$) stretching as well as deformation vibrations (NH$_2$, 1630–1578 cm$^{-1}$) are present together with the pattern of fingerprint region corresponding to the three coordinated molecules of $en$ (the full IR spectrum is available in Additional file 1: Figure S1).

The temperature dependence of the effective magnetic moment (for details see Additional file 1: Figure S2) revealed weak antiferromagnetic interactions. The effective magnetic moment of 1a at room temperature was 2.23 B.M. and it is gradually decreased to 1.84 B.M. as the temperature was reduced to 2 K. Its value was higher than expected for the spin-only value of 1.73 B.M. for $S=1/2$, but similar to the value of 2.25 B.M. obtained for K$_3$ [Fe(CN)$_6$] [63]. Fitting of the reciprocal susceptibility (see Additional file 1: Figure S3) above 50 K by Curie-Weiss law gave $g = 2.67$ and $\Theta = -19$ K for $S = 0$ and $S = 1/2$ for Co$^{III}$, and Fe$^{III}$, respectively. The higher values of $g$-factors have been previously observed for other low-spin Fe$^{III}$ complexes as well [64].

**Thermal behavior of [Co(en)$_3$][Fe(CN)$_6$]·2H$_2$O (1a) – a general overview**

The TG and DSC curves of 1a are displayed in Figure 5. TG curve of 1a reveals two separable steps of the thermal decomposition. The first weight loss occurs in the temperature range of 50–80°C and it is accompanied by endothermic effect with the minimum at 80°C, as can be seen on DSC curve (Figure 5). Experimental weight loss (5.6%) is in good agreement with the calculated one (5.5%) corresponding to the release of 1.5 crystal water molecules from the formula unit of 1a and thus, yielding the complex [Co(en)$_3$][Fe(CN)$_6$]·1/2H$_2$O (1b), as confirmed by chemical and single crystal X-ray analyses. The hemihydrate 1b is thermally stable within the temperature interval of 72–187°C. The second step of the thermal decay is observed in the temperature range of 187–420°C, and involves continual and complete sample decomposition. Based on the course of DSC curve, it can be stated that at least three processes take place: (i) a weak exothermic process with the maximum at 208°C, (ii) an endothermic process with the minimum at 214°C and (iii) a strong exothermic effect with the maximum at 354°C. The sample weight loss corresponding to the second step was found to be 61.7%. It can be assigned to elimination of the remaining water content, all molecules of ethylenediamine as well as all CN$^-$ ligands and/or oxidation of the transition metal ions yielding a spinel-type phase with the general chemical composition of Co$_{1.5}$Fe$_{1.5}$O$_4$ (calculated weight loss 62.1%).
The complex $\text{[Co(CN)$_5$]}^2$ and $\text{[FeIII(CN)$_5$]}^2$ were identified during recently published in Ref. [52], the decomposition of 1a occurs at lower temperature in our case, which can be associated to different experimental conditions, and moreover, CoFe$_2$O$_4$ only was determined as the final decomposition product [56]. Unstable intermediates $\text{[FeII(μ-NC)CoIII(CN)$_5$]}$, $\text{[FeIII(H$_2$NCH$_2$CH$_3$)$_2$μ-NC)CoII(CN)$_5$]}$, and $\text{[FeIII(CO)$_5$][CoIII(CN)$_5$]}$ were identified during this complicated decomposition. The detailed description of the above-mentioned processes with identification of the intermediates by XRD method, Mössbauer spectroscopy and transmission electron microscopy (TEM) will be discussed below mainly from the chemical point of view (vide infra).

Chemical, structural and spectral characterization of $\text{[Co(en)$_3$][Fe(CN)$_5$]}^2$·2H$_2$O (1b) formed in the first decomposition step
The complex $\text{[Co(en)$_3$][Fe(CN)$_5$]}^2$·1/2H$_2$O (1b), as it was already mentioned, can be obtained as a stable intermediate by both dynamic or static heating of the dihydrate 1a up to 130°C (Table 4). The empirical formula of 1b was deduced from the elemental analysis results and well corresponds to the weight loss on the TG curve (Figure 5). The parameters of Mössbauer spectrum of 1b ($\delta = -0.15$ mm/s and $\Delta E_Q = 0.98$ mm/s) exhibit small changes as compared to the corresponding values of 1a ($\delta = -0.17$ mm/s and $\Delta E_Q = 0.85$ mm/s). Generally, the found hyperfine parameters refer to the presence of Fe(III) cations in the low-spin state in both complexes. Small increase in the quadrupole splitting value is evidently related to a small decrease in the symmetry of the iron atom surroundings as a consequence of the topotactic dehydration process. Similar findings, connecting with the variations in Mössbauer parameters depending on a number of crystal water molecules presented in the structure, were previously observed for a series of $\text{[M}_3[\text{Fe(CN)}_6]_2\cdot n\text{H}_2\text{O}}$ complexes (M = Ni, Mn, Co, Cu, Cd, n can rise up to 14) [61]. There is only very small difference in measured IR spectra between 1a and 1b, because all above described absorption bands for 1a are also present in the spectrum of 1b (Figure 4).

The single crystal character is preserved during the dehydration process of 1a to 1b what is, generally, a very rare phenomenon among coordination compounds although it is quite common for simple salts, e.g. K$_{0.33}$CoO$_2$·0.4H$_2$O [65], manganese(II) formate [66] or FePO$_4$ [67]. To our knowledge, the single crystal dehydration process was reported only for a series of polymeric compounds $\text{[M(H$_2$O)$_2$CoO$_2$]}$ [bipy$_2$]·H$_2$O$_n$, (M = Co, Ni, Fe) [68], and $\text{[Ni(en)$_3$][Fe(CN)$_5$]}$·2H$_2$O [60] up to date.
The molecular structure of the hemihydrate \(1b\) (Figure 1, Tables 1 and 2) is analogous to that of the original dihydrate \(1a\), since it is composed of the same complex cations and anions. Main, but not significant, structural variances between \(1a\) and \(1b\) are caused by the presence of different number of crystal water molecules. Thus, the dehydration process is accompanied by small shifts only in the positions of the respective \([\text{Co(en)}_3]^{3+}\) and \([\text{Fe(CN)}_6]^{3-}\) ions as can be deduced from the mean values of the Co⋯Fe distances to the six nearest neighbors which were found to be 6.32(4) and 6.22(4) Å in the crystal structures of \(1a\), and \(1b\), respectively. Both \(1a\) and \(1b\) crystallize in the monoclinic system in related space groups (i.e. \(P2_1/n\) for the dihydrate and \(P2_1/c\) for the hemihydrate), but with the different unit cell orientations towards the presented molecules. The relationship between two unit cell settings can be expressed by the equation \((a_H, b_H, c_H) = (010, 100, 00-1)\) \((a_D, b_D, c_D)\) stand for cell parameters of the hemihydrate (H), and dihydrate (D), respectively. It should be noted that the monoclinic angles in both unit cells \([\beta_D = 91.982(4)^\circ\) and \(\beta_H = 90.15(1)^\circ]\) display only minor deviation from the right angle. As expected, the unit cell dimensions of the hemihydrate \(1b\) are somewhat shorter in lengths as compared to the dihydrate \(1a\). Therefore the dehydration process from the dihydrate \(1a\) to the hemihydrate \(1b\) can be considered as topotactic because of minimal geometric changes (less than 4%) and minimal atomic and molecular movements (change of each intra-/intermolecular distances < 4.2 Å) [53].

Despite considerable similarity between both structures, also some differences can be found. The partial dehydration caused conformational change within the \([\text{Co(en)}_3]^{3+}\) cations. While the \(\Lambda\delta\delta\delta\) (and \(\Delta\lambda\lambda\lambda\)) conformation was observed in \(1a\), the \(\Lambda\lambda\delta\delta\) (and \(\Delta\delta\lambda\lambda\)) conformation was found in \(1b\) (Figure 6). It can be assumed that these conformational variations are induced by changes in the hydrogen bonding interactions (see below) as was previously suggested in conformation analysis of \([\text{M(en)}_3]^{3+}\) (M = CoIII, CrIII) [54]. Moreover, together with the conformational changes within the \([\text{Co(en)}_3]^{3+}\) cations, the shortening in the Co–N bond lengths in the hemihydrate \(1b\) (1.956(2)–1.968(2) Å) were found as compared to those in \(1a\) (1.955(2)–1.981 (2) Å). However, all these values are comparable to those determined for the same cation in similar systems (1.97 (7) Å) [33].

Figure 2 Part of the crystal structure of \([\text{Co(en)}_3][\text{Fe(CN)}_6]\cdot2\text{H}_2\text{O}\) (1a) showing selected non-covalent contacts (dashed lines). The CH\(_2\) groups of the ethylenediamine ligands are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.
with \([\text{Fe(CN)}_6]^{3-}\) of the dihydrate the crystal structure of mentioned non-bonding interactions is slightly lower, this general statement, the number of the above-within the crystal structures. Thus, as a consequence of gen bonds and other non-covalent contacts presented.

$\text{EQ} = 0.60 \text{ mm/s}$ can be ascribed to a high spin Fe(III) environment in tetrahedral coordination [70]. The presence of three broadened Fe(II) doublets (2.53 mm/s) manifest a very low symmetry of the Fe(II) environment as expected for the coordination number 5 environment as expected for the coordination number 5.

Generally, it can be anticipated, that the topotactic dehydratation may influence significantly an extent of hydrogen bonds and other non-covalent contacts presented within the crystal structures. Thus, as a consequence of this general statement, the number of the above-mentioned non-bonding interactions is slightly lower, and moreover, they are moderately shorter than those in the crystal structure of 1a. While in the crystal structure of the dihydrate 1a, the water molecules are connected with \(\text{Fe(CN)}_6^{3-}\) anions via hydrogen bonds of the type O–H⋯N and O–H⋯O, the O–H⋯O hydrogen bond is absent in the crystal structure of 1b (Table 3, Figure 7).

The magnetic properties of the hemihydrate 1b (see Additional file 1: Figure S2 and S3) are similar compared to those for the dihydrate 1a. Fitting of the temperature dependence of reciprocal susceptibility above 50 K by Curie-Weiss law gave \(\chi = 2.77\) and \(\Theta = -18\) K indicating slightly weaker antiferromagnetic interaction in comparison with 1a. The effective magnetic moment of 1b at room temperature is similar to the value for 1a, but a small difference becomes visible when the temperature declines below 50 K (Additional file 1: Figure S2) where the values of \(\mu_{\text{eff}}\) for 1b are slightly higher than those for 1a and thus, indicating weaker antiferromagnetic interactions. Such observation is in accordance with the topotactic dehydration process which reduces the number of intra-molecular interactions as was observed in the crystal structure of 1b. The completed CIF files for 1a and 1b can be found as Additional files 2, and 3, respectively.

### Chemical, structural and spectral characterization of the intermediates formed during the second and third decomposition steps

To explain the unexpected exothermic effects in DSC curves accompanying the evolution of molecules of en at higher temperatures and generally, to understand the structure and chemical composition of intermediates formed during the appropriate stage of the thermal treatment, the complex 1a was heated dynamically in conditions of the DSC experiment up to the selected temperatures and the samples were analyzed consequently by Mössbauer and IR spectroscopy and elemental analysis. The results obtained from these measurements together with the proposed composition of conversion intermediates are summarized in Table 4. The suggested decomposition model for 1a is depicted in Scheme 1.

When 1a was heated up to 240°C (sample 2), the color of sample turned from orange to green. It was demonstrated by DSC that this solid underwent an exothermic effect with the maximum at 208°C followed by an endothermic effect with the minimum at 214°C. The Mössbauer spectrum of 2 consists of four doublets which correspond to iron-containing species in two different oxidation states (see Figure 3 and Table 4). Three doublets with \(\delta\) values ranging from 1.02 to 1.31 mm/s correspond clearly to the high spin Fe(II) atoms [69,70]. The high values of quadrupole splitting parameters (1.95–2.53 mm/s) manifest a very low symmetry of the Fe(II) environment as expected for the coordination number 5 [69]. The presence of three broadened Fe(II) doublets varying in the values of \(\Delta E_Q\) is probably related to the various degrees of the deformation of the iron(II) environment. The most populated doublet (\(\delta = 0.22\) mm/s; \(\Delta E_Q = 0.60\) mm/s) can be ascribed to a high spin Fe(III) environment in tetrahedral coordination [70]. The increase of the isomer shift in comparison with 1a or 1b can be attributed to the iron spin transition from low to...
high spin as well as to the different coordination mode of cyanide ion to Fe(III) (Fe$^{II}$–CN in 1a,b, Fe$^{III}$–NC in 2) [50]. The results of Mössbauer spectroscopy give an evidence for the surprising change of the spin state of all iron atoms between 130 and 240°C as all the spectral components correspond to the high-spin states. Moreover, the presence of divalent iron indicates a central atom reduction which accompanies oxidation of CN$^-$ to (CN)$_2$. The formed cyanogen can react with two molecules of en which are also liberated during this thermolytic step and one bicyclic molecule of bis(Δ$^2$-2-imidazolinyl) [71] could be formed as a potential product of the decomposition (see Scheme 1). All the mentioned experimental results can be explained by the formation of the bridging [Fe$^{III}$(en)$_2$(μ-NC)Co$^{III}$(CN)$_4$] complex from the hemihydrate 1b (see step II in Scheme 1) what is in accordance with the preference of HS Fe(II) to be coordinated in weaker ligand field provided by N-donor atoms rather than C-donor atoms. It seems that the complete dehydration induces a drastic rearrangement of the environments of both central atoms related to the evolution of half molecule of cyanogen and one molecule of en from the formula unit of 1b, which is probably reflected on the DSC curve by the mentioned exo-effect at 208°C. Nevertheless, similar process of deamination has been described previously on
other systems containing [Co(en)_3]^{3+} and it was always accompanied by a strong endo-effect above 200°C on the DSC curve [72]. Thus, the following endo-effect at 214°C on the DSC curve could be ascribed to the liberation of en as well.

The simultaneous presence of the high spin Fe(II) and Fe(III) species in sample 2 can be related to the partial transformation of [Fe^{II}(en)_2(μ-NC)Co^{III}(CN)_4] to [Fe^{II}(NH_2CH_2CH_3)_2(μ-NC)_2Co^{II}(CN)_3] (see step III in Scheme 1). This charge transfer process has been previously observed and confirmed in many Fe^{II}–CN–Co^{III} species (light-induced magnetization changes) [19-23] and here, it is more pronounced at higher temperature as clearly seen from the comparison of the Fe(II)/ΣFe ratio of 0.34 found in sample 2 heated up to 240°C with that observed in sample 3 heated up to 300°C (0.18; see Table 4

**Table 4** Room temperature Mössbauer parameters and the corresponding elemental analyses of complex 1a as well as the samples prepared by its dynamic heating up to 130–600°C

| Sample number | T [°C] | phase   | δ [mm/s] | ΔE_j [mm/s] | H_{hyp} [T] | RA [%] | Elemental analyses [%] | Assignment |
|---------------|-------|---------|----------|-------------|-------------|--------|------------------------|------------|
| 1a            | 25    | LS Fe(III) | −0.17    | 0.85        | –           | 100    | 34.4 29.8 5.5           | [Co^{III}(en)_3][Fe^{III}(CN)_6]·2H_2O |
| 1b            | 130   | LS Fe(III) | −0.15    | 0.98        | –           | 100    | 36.0 31.2 5.4           | [Co^{III}(en)_3][Fe^{III}(CN)_6]·½H_2O |
| 2             | 240   | HS Fe(II)  | 1.17     | 2.25        | 13.0        | 31.3   | 33.2 3.9                | [Fe^{II}(en)_2(μ-NC)Co^{III}(CN)_4] |
| 3             | 300   | HS Fe(II)  | 1.14     | 2.49        | –           | 18.4   | 26.8 31.9 3.0           | [Fe^{II}(en)_2(μ-NC)Co^{III}(CN)_4] |
| 4             | 350   | HS Fe(II)  | 0.26     | 0.43        | –           | 55.7   | 19.9 22.8 2.0           | [Fe^{II}(NH_2CH_2CH_3)_2(μ-NC)_2Co^{III}(CN)_3] |
| 5             | 400   | HS Fe(II)  | 0.31     | 0.76        | –           | 100    | 0 0 0                   | CoFe_2O_4 (SP) |
| 6             | 450   | HS Fe(II)  | 0.31     | 0.82        | –           | 46.8   | 0 0 0                   | CoFe_2O_4 (SP) |
| 7             | 600   | HS Fe(II)  | 0.31     | 0.53        | –           | 3.4    | 0 0 0                   | CoFe_2O_4 (SP) |

(LS) low-spin state, (HS) high-spin state, (SP) superparamagnetic particles, (RA) relative abundance.
and Figure 3). In this third decomposition step we assume the participation of atmospheric oxygen and gradual evolution of NO$_X$. This assumption is in accordance with the N/C ratio decrease between 240 (0.94) and 300°C (0.84; see Table 4). The step III is manifested in DSC curve through a long endo-effect with the minimum at 214°C or rather long exo-effect in the temperature range of 220–300°C without specified maximum (see Figure 5). It is worth to mention that both samples 2 and 3 revealed a drastic lowering of conductivity compared to hemihydrate 1b, which is in line with the presence of bridging ligands between Co and Fe central atoms in the dinuclear species.
IR spectra recorded for the intermediates in sample 2 and 3 (230 and 265°C, Figure 4) confirmed proposed thermal decomposition mechanism. The $\nu$(C≡N) stretching vibration is significantly governed by the electronegativity, oxidation state and coordination number of the metal central atom directly bonded to the cyanide group. Thus, the formation of cyanido-bridged species is accompanied by a significant broadening of the $\nu$(C≡N) bands observed in IR spectra. Furthermore, the shift of the peak at 2113 cm$^{-1}$ toward higher wave numbers (2113 $\rightarrow$ 2127 $\rightarrow$ 2132 cm$^{-1}$ for 150 $\rightarrow$ 230 $\rightarrow$ 265°C) documents the oxidation state changes and could be assigned to $\nu$(Fe$^{II}$–CN–Co$^{III}$). The intensity of this vibration band decreases with higher temperature which indicates absence of such type of coordination above 265°C. On the other hand, the shift of the peak at 2104 cm$^{-1}$ toward lower wave numbers with increasing temperature (2104 $\rightarrow$ 2062 $\rightarrow$ 2066 cm$^{-1}$ for 150 $\rightarrow$ 230 $\rightarrow$ 265°C) corresponds to $\nu$(Co$^{III}$–CN–Fe$^{III}$) [50]. This observation confirms the proposed decomposition mechanism concerning increasing amount of [Fe$^{III}$(en)$_3$][Fe$^{III}$(CN)$_6$]$_2$(μ-CN)$_2$Co$^{II}$(CN)$_3$ at higher temperature (see step III in Scheme 1 and Table 4) and it indicates that Co$^{II}$–CN–Fe$^{III}$ is the most probable coordination bridge in [Fe$^{III}$(NH$_2$CH$_2$CH$_3$)$_2$(μ-CN)$_2$Co$^{II}$(CN)$_3$]. Although non-linear coordination mode of bridging cyanide in di/polynuclear complexes is known, the suggested structure of [Fe$^{III}$(NH$_2$CH$_2$CH$_3$)$_2$(μ-CN)$_2$Co$^{II}$(CN)$_3$] requires two cyanide bridges of that type. Such coordination tension could be reduced if the formation of a structure with the cyclic tetranuclear {Fe$_2$Co$_2$(CN)$_4$} core is considered. Moreover, compounds with similar core-structure have been described recently [73]. Another possibility is the formation of a polymeric structure with μ$_3$-CN coordination mode found in the case of several Cu(I)–Zn(II) complexes.

**Scheme 1** Suggested scheme of thermal decomposition of [Co$^{III}$(en)$_3$][Fe$^{III}$(CN)$_6$]•2H$_2$O (1a) during dynamic heating in air atmosphere. (Endo stands for endo-effects, while Exo for exo-effects).
the percentage of Fe(II) and Fe(III) species, their phase composition is similar from the qualitative viewpoint as evident from hyperfine parameters of Mössbauer spectra. The next principal chemical change in the chemical composition of the samples takes place after heating up to 350°C (sample 4). This fourth reaction step is reflected on the DSC curve at 335°C by a shoulder of exo-effect at 354°C and documented also by a considerable diminution of both C and N contents (see Table 4). In Mössbauer spectrum of the sample 4 (see Figure 3) heated up to 350°C, there are no indications of the divalent iron species in contrast to the room temperature spectra of samples 2 and 3. On the other hand, a new high-spin Fe(III) phase with $\delta = 0.46$ mm/s and quadrupole splitting $\Delta EQ = 1.22$ mm/s appears in the spectrum along with the residual doublet ascribed to $[\text{Fe}^{\text{III}}(\text{NH}_2\text{CH}_2\text{CH}_3)(\mu-\text{NC})_2\text{Co}^{\text{II}}(\text{CN})_3]$ as its hyperfine parameters are almost unchanged compared to the spectrum of sample 3. The hyperfine parameters of the former species are in a very good accordance with those observed for iron complexes with pentacoordinated high spin Fe(III) environments [74]. Thus, this new phase with the low symmetry of iron environment, which is manifested by a high value of quadrupole splitting, can be ascribed to $[\text{Fe}^{\text{III}}(\text{NH}_2\text{CH}_2\text{CH}_3)(\mu-\text{NC})_2\text{Co}^{\text{II}}(\text{CN})_3]$ to $[\text{Fe}^{\text{III}}\text{Co}^{\text{II}}(\text{CN})_3]$ (see step IV in Scheme 1), their experimental identification using evolved gas analysis (EGA) may be ambiguous due to the negative role of atmospheric nitrogen and oxygen. Nevertheless, previous decomposition studies of other complexes with en, e.g. $[\text{Ni}(en)_3](\text{ox})$ [75] using EGA showed that en is decomposed to a mixture of $\text{H}_2$, $\text{CO}/\text{CO}_2$, $\text{N}_2$ and $\text{CH}_2=\text{CH}_2$ in an inert atmosphere. Thus, the decomposition of ethylamine in air may involve similar or more oxygen containing species such as $\text{H}_2\text{O}$, $\text{CO}$, $\text{CO}_2$, $\text{N}_2$ or $\text{NO}_x$.

Characterization of the final decomposition product – the fifth decomposition step

In accordance with TG data, decomposition process is completed in dynamic conditions at 420°C. As mentioned above, the overall weight loss corresponds well with the final formation of the $\text{M}_3\text{O}_4$ ($\text{M} = \text{Fe}, \text{Co}$) phase(s) which is in accordance with the absence of $\nu(\text{C} \equiv \text{N})$ stretching vibration bands in IR spectrum (Figure 4, 450°C). Taking into account the starting molar ratio of $\text{Fe}/\text{Co} = 1/1$, various combinations of several oxides (CoFe$_2$O$_4$, Fe$_2$O$_3$, Fe$_3$O$_4$ polymorphs, Co$_3$O$_4$, FeCo$_2$O$_4$) come on force to express the phase composition of the final product. The isomer shift values in room temperature Mössbauer spectra of the final decomposition products formed after dynamic heating of 1a up to 450 and 600°C (samples 5, 6 and 7, see Table 4 and Figure 8) unambiguously exclude the presence of divalent iron (Fe$_2$O$_4$, FeCo$_2$O$_4$) in the iron oxide phase [76]. The spectra of the samples 5 and 6 heated up to 400 and 450°C display a broadened doublet as a prevailing component, which can be ascribed to superparamagnetic nanoparticles. Superparamagnetic character of the spectra disallows the identification of iron(III) oxide phase (CoFe$_2$O$_4$ vs. $\gamma$-Fe$_2$O$_3$ vs. $\alpha$-Fe$_2$O$_3$) in all samples. In the spectrum of sample 6 heated to 450°C, the prevailing doublet is accompanied by a completely magnetically split sextet which becomes the major signal observed in the spectrum of sample 7 prepared by heating of 1a up to 600°C (see Figure 8). This reduction of the ratio between the intensity of the doublet (superparamagnetic particles) and sextet manifests the formation of larger particles (~50 nm) due to the proceeding crystallization process. The room temperature spectrum of sample 7 can be fitted by two six-line hyperfine patterns with the nearly the same isomer shift (0.29 and 0.37 mm/s) and hyperfine magnetic fields of 48.6 and 51.4. Generally the isomer shift parameters are closed to those reported for CoFe$_2$O$_4$ [77] and $\gamma$-Fe$_2$O$_3$ (0.27 mm/s) [78] or hematite, $\alpha$-Fe$_2$O$_3$ (0.38 mm/s) [78]. Two sextets differing in isomer shift and hyperfine magnetic field can be ascribed to Fe(III) ions located at the tetrahedral ($T_d$), $\delta = 0.37$ mm/s, $H_{hyp} = 51.4$ T, and octahedral

![Figure 8 Room temperature Mössbauer spectra of the decomposition products prepared by dynamic heating of 1a up to 450°C (sample 6) and 600°C (sample 7).](http://journal.chemistrycentral.com/content/7/1/28)
(O\textsubscript{h}), \( \delta = 0.29 \) mm/s, \( H\text{hyp} = 48.6 \) T, sites of the partially inverse spinel structure of CoFe\textsubscript{2}O\textsubscript{4}. In comparison with bulk CoFe\textsubscript{2}O\textsubscript{4}, (51.2 T for \( T_{\text{d}} \)-site, 55.0 T for \( O_{\text{h}} \)-site) the values of \( H\text{hyp} \) of prepared CoFe\textsubscript{2}O\textsubscript{4} nanoparticles (42.6 T for sample 6, 48.6 and 51.4 T for sample 7) are smaller due to their lower crystallinity [79].

In Figure 9, the XRD spectrum of sample 7 is shown, which consists of two sets of peaks corresponding to two spinel phases. The presence of \( \gamma - \text{Fe}_{2}O_{3} \) or \( \alpha - \text{Fe}_{2}O_{3} \) is clearly excluded because the first set of peaks corresponds to CoFe\textsubscript{2}O\textsubscript{4} phase [77] (marked with asterisks) and the second pattern belongs to Co\textsubscript{3}O\textsubscript{4} (labeled with short vertical lines). According to the XRD data, the molar ratio between these two phases was found to be 2.44 : 1 (CoFe\textsubscript{2}O\textsubscript{4} : Co\textsubscript{3}O\textsubscript{4}) what is in accordance with the proposed stoichiometry of both phases.

To confirm the inverse spinel phase formed during the heating of 1a up to 600°C and reveal the magnetic structure, the in-field Mössbauer spectrum of sample 7 was recorded (Figure 10, Table 5). It consists of two overlapping six-line hyperfine patterns corresponding to Fe(III) in \( T_{\text{d}} \)- and \( O_{\text{h}} \)-sites of spinel lattice (partial separation of both patterns). The data were successfully fitted with two sextets having the \( \delta = 0.38 \) mm/s, \( \Delta E_{Q} = -0.02 \) mm/s and \( H\text{hyp} = 52.6 \) T corresponding to Fe(III) in \( T_{\text{d}} \)-site and \( \delta = 0.54 \) mm/s, \( \Delta E_{Q} = -0.08 \) mm/s and \( H\text{hyp} = 49.0 \) T for Fe(III) in \( O_{\text{h}} \)-site, respectively. The degree of conversion for inverse spinel, \( x \), which identifies its formula Fe(III)\textsubscript{1-x}[Co(II)\textsubscript{x}Fe(III)\textsubscript{2-x}]O\textsubscript{4} (brackets indicate ions at \( O_{\text{h}} \)-site), can be calculated on the basis of the relative contribution of individual \( T_{\text{d}} \)- and \( O_{\text{h}} \)-site sextets. The value of \( x \) was obtained from the equation \( x = 2k(1 + k) \) where \( k \) is the ratio between Fe(III) ions in the tetrahedral and octahedral sublattices calculated from the ratio between the areas of individual sextets corresponding to \( T_{\text{d}} \)- and \( O_{\text{h}} \)-sites. The obtained value of \( x = 0.9 \) indicates the formation of partially/almost fully inverse spinel structure Fe(III)\textsubscript{0.9}Co(II)\textsubscript{0.1}[Co(II)\textsubscript{0.9}Fe(III)\textsubscript{1.1}]O\textsubscript{4}. The determination of the degree of inversion at low temperature in external magnetic field is more accurate in comparison with room temperature spectra (Figure 8) because the applied magnetic field better separates the \( T_{\text{d}} \)- and \( O_{\text{h}} \)-site contributions (sextets) and the low temperature reduces the vibrations of the lattice and/or the Mössbauer nucleus (significantly influence the ration between the \( T_{\text{d}} \)- and \( O_{\text{h}} \)-signals).

The intensities of 2nd and 5th lines are lower than expected for a thin sample with randomly oriented magnetic moments in the absence of magnetic field (ideally 3:2:1:2:3) which is characteristic for the materials in ferromagnetic and/or ferrimagnetic state and which corresponds to the partial alignment of the iron magnetic moments in the direction of the external magnetic field. If the iron magnetic moment were completely aligned, the 2nd and 5th lines would be completely vanished. Thus, the presence of the 2nd and 5th lines in the spectrum points out to the canting of Fe(III) spin in CoFe\textsubscript{2}O\textsubscript{4} particles with respect to the direction of the external magnetic field. Based on the comparison of the areas corresponding to 2, 5 and 1, 6 lines, the average spin-canting angle, \( \theta \), was evaluated on the basis of the formula \( \theta = \arccos\frac{[4-s]}{[4+s]}^{1/2} \) [80] where \( s = A_{2,5}/A_{3,6} \) and was calculated to be 30.3° (from both \( T_{\text{d}} \)- and \( O_{\text{h}} \)-sites). The thickness of the spin-canted surface layer of the sample was not deduced because the shape of prepared particles was not considered as spherical.

Figure 9 XRD pattern of the sample prepared by heating of 1a up to 600°C. (*) CoFe\textsubscript{2}O\textsubscript{4}, (I) Co\textsubscript{3}O\textsubscript{4}. 
The morphology of the product formed by heating of \( \text{1a} \) up to 600°C (sample 7) is clearly visible on TEM pictures (Figure 11), which confirm the nanocomposite structure of the \( \text{CoFe}_2\text{O}_4 - \text{Co}_3\text{O}_4 \) particles. But these nanoparticles, taken directly after the thermal decomposition, form agglomerates and are not well-dispersed and thus, their median size based on TEM analysis was not calculated.

**Conclusions**
The thermal decomposition of \([\text{Co}(\text{en})_3][\text{Fe(CN)}_6]\)·2H\(_2\)O (\( \text{1a} \)) in air atmosphere was monitored by TG/DSC techniques. Seven samples were prepared by annealing \( \text{1a} \) at selected temperatures, which were completely characterized by elemental analyses, IR and \( ^{57}\text{Fe} \) Mössbauer spectroscopies with the aim to elucidate the decomposition mechanism. It has been found that the topotactic dehydration of \( \text{1a} \) led to the formation of the hemihydrate \([\text{Co}(\text{en})_3][\text{Fe(CN)}_6]\)·1/2H\(_2\)O (\( \text{1b} \)), which was consequently decomposed in next four steps, going through the \([\text{Fe}^{II}(\text{en})_2(\mu-\text{NC})\text{Co}^{III}\text{CN}_3]\), \([\text{Fe}^{III}(\text{NH}_2\text{CH}_2\text{CH}_3)_2(\mu-\text{NC})\text{Co}^{III}\text{CN}_3]\) and \([\text{Fe}^{III}\text{Co}^{III}\text{CN}_3]\) intermediates, leading to \( \text{CoFe}_2\text{O}_4 - \text{Co}_3\text{O}_4 \) nanocomposite particles at as the final product (confirmed by TEM). It has been shown that a relatively small change regarding the heating gradient (5°C/min in this work versus 10°C/min in Ref. 52) may substantially influence the composition and particle size of the final product. Moreover, from a general point of view, the obtained results also revealed that the thermal decomposition of such a simple salt as \([\text{Co}(\text{en})_3][\text{Fe(CN)}_6]\)·2H\(_2\)O involves a relatively complicated mechanism driven mainly by the reaction conditions (such as the heating gradient and air atmosphere) and is composed by several overlapping steps and resulting in the formation of interesting nanoparticles with a nanocomposite structure of two magnetically different phases. It may be anticipated that the modulation of their properties would be possible by the exact control of the temperature (gradient or prolonged heating or amine-ligand substitution) and further investigation of magnetic properties of such system would be very interesting and helpful.

**Experimental**
**Materials and reagents**
\( \text{K}_3[\text{Fe(CN)}_6] \) (Merck) and \( \text{N,N}'-\text{dimethylformamide} \) (Lachema Brno) were purchased from commercial sources and used as received. \([\text{Co}(\text{en})_3]\text{Cl}_3\)·3H\(_2\)O was prepared by a slightly modified procedure described in the literature [81].

**Synthesis**
\([\text{Co}(\text{en})_3][\text{Fe(CN)}_6]\)·2H\(_2\)O (\( \text{1a} \)).

0.39 g (1 mmol) of \([\text{Co}(\text{en})_3]\)\( \text{Cl}_3\)·3H\(_2\)O and 0.32 g (1 - mmol) \( \text{K}_3[\text{Fe(CN)}_6] \) were added into 20 ml of \( \text{N,N}'-\text{dimethylformamide} \) (DMF) with stirring and refluxed for 1 h. The yellow-orange precipitate formed in the reaction mixture and the color of the solvent changed into light-green. The solid was filtered off, and consequently dissolved in 30 ml of warm water (60°C). The solution was left to stand at room temperature. Yellow-orange

**Table 5** Hyperfine parameters of in-field Mössbauer spectrum of sample 7 at 5 K and in external field 5 T

| Position of the Fe\(^{III}\) ions | \( \delta \) ± 0.01 (mm/s) | \( \Delta E_Q \) ± 0.01 (mm/s) | \( B_{\text{eff}} \) ± 0.3 (T) | \( \Gamma \) ± 0.01 (mm/s) | RA ± 3% | \( A_{2,5}/A_{3,4} \) | Canting angle (°) | Average canting angle of both sites (°) |
|---|---|---|---|---|---|---|---|---|
| T-site | 0.38 | -0.02 | 52.6 | 0.54 | 45 | 0.579 | 30.2 | 30.3 |
| O-site | 0.54 | -0.08 | 49.0 | 0.63 | 55 | 0.589 | 30.4 | 30.5 |

Where \( \delta \) is center shift, \( \Delta E_Q \) is quadrupole splitting, \( B_{\text{eff}} \) is effective magnetic field, \( \Gamma \) is line width and RA is the relative area of individual sextets. Furthermore, \( A_{2,5} \) and \( A_{3,4} \) are the intensities of the second/fifth, and third/fourth lines, respectively.
crystals were obtained by slow evaporation of the solvent after several hours. They were filtered off, washed with small amount of cold water and dried on air (yield 55%). Anal. calc. for C₁₂H₂₈N₁₂CoFeO₂: C, 29.8; H, 5.8; N, 34.7%. Found: C, 30.2; H, 5.5; N, 34.4%. IR: 3381 bm, 3279 s, 3232 bs, 3095 bs, 2117 vs, 2107 vs, 1630 m, 1609 m, 1578 m, 1464 m, 1399w, 1334 m, 1289 w, 1156 m, 1143 m, 1051 m, 763 w, 580 m.

Physical measurements
Elemental analyses (C, H, N) were performed on a Flash EA 1112 Elemental Analyser (ThermoFinnigan). Thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements of 1a were performed in static air atmosphere under dynamic heating conditions with a sample weight of 6–8 mg and heating rate 5°C/min. DSC measurements were performed in the range of 20–400°C on a DSC XP-10 analyser (THASS, GmbH) and TG curve was measured between 20–500°C on a TG XP-10 instrument (THASS, GmbH). To monitor the intermediates of the thermal decay, the samples were prepared in conditions of DSC measurement by dynamic heating up to the selected temperatures, with the heating rate of 5°C/min and consequently analyzed by suitable techniques. The transmission ⁵⁷Fe Mössbauer spectra were collected at 300 K in a constant acceleration mode.
with a $^{57}$Co(Rh) source. The final decomposition product was also analyzed at 5 K in zero external magnetic field and at 5 K in an external magnetic field of 5 T, applied parallel to the X-ray direction using a cryogenic system of Oxford Instruments. The isomer shift values were calibrated against metallic α-Fe. In-field Mössbauer spectra were fitted by means of the Lorentzian line shapes using the least squares method featured in the MossWinn computer program. FT IR spectra were measured on a Nexus 670 FT-IR (Thermo Nicolet) spectrophotometer using KBr pellets in the wavenumber range of 400–4000 cm$^{-1}$ at temperatures 25, 150, 230, 265 and 450°C.

The transmission electron microscopy was performed on a JEOL JEM-2010 instrument (LaB$_6$ cathode; accelerating voltage of 200 kV; point-to-point resolution 0.19 nm) to consider the particle size and structure of the final spinel phase. A drop of high-purity distilled water, containing the ultrasonically dispersed particles, was placed onto a holey-carbon film supported by a copper-mesh TEM grid and dried in air at room temperature.

**X-ray structure determinations and refinements**

X-ray single crystal diffraction experiments for both 1a and 1b were carried out on a four circle κ-axis Xcalibur2 diffractometer at 100(2) K equipped with a CCD detector Saphire2 (Oxford Diffraction). The CrysAlis software package [82] was used for data collection and reduction. The structures were solved by the SIR97 program [83] incorporated within the WinGX program package [84]. All non-hydrogen atoms of 1a and 1b were refined anisotropically by the full-matrix least-squares procedure [85], with weights: $w = 1/[(σ^2(F_0^2) + (0.0633P)^2)]$ for (1a) and $w = 1/[(σ^2(F_0^2) + (0.0605P)^2 + 0.3587P)]$ for (1b), where $P = (F_0^2 + 2F_c^2)/3$. Hydrogen atoms were found in the difference Fourier maps, nevertheless these were modeled using a riding model, except for those belonging to crystal water molecules, which parameters were fixed. The structures of 1a and 1b, depicted in Figures 1, 2, 6 and 7, were drawn using the Diamond software [86]. X-ray powder diffraction pattern of the final decomposition product was recorded using a PANalytical X’Pert MPD device (iron-filtered CoK$_\alpha$ radiation: $\lambda = 0.178901$ nm, 40 kV and 30 mA) in Bragg-Brentano geometry, and equipped with X’Celerator detector. Powdered sample was spread on zero-background single-crystal Si slides and scanned in continuous mode (resolution of 0.017° 2 Theta, scan speed of 0.005° 2 Theta per second) within the angular range 10–120°. The acquired patterns were processed (i.e., phase analysis and Rietveld refinement) using X’ Pert HighScore Plus software (PANalytical, The Netherlands), in combination with PDF-4+ and ICSD databases (ICSD collection codes are: Co$_3$O$_4 = 63165$, CoFe$_2$O$_4 = 98553$).

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**Acknowledgements**

The authors gratefully thank the Operational Program Research and Development for Innovations - European Regional Development Fund (CZ.1.05/2.1.00/03.0058), Operational Program Education for Competitiveness-European Social Fund (CZ.1.07/2.3.00/20.0107) of the Ministry of Education, Youth and Sports of the Czech Republic. The authors also acknowledge the financial support from the Grant Agency of the Czech Republic (Grant No. P207/11/0841). We also thank to J. Filip for XRD experiments data and to L. Machala and J. Cuda for the fitting of Mössbauer spectra. JC thanks grant APVV-0014-11 for partial financial support.

**Authors’ contributions**

MMW synthesized all samples and made substantial contributions to the data collection and analysis. BD made substantial contributions to the survey results, data analysis/interpretation and drafting the manuscript. ZT performed single-crystal diffraction experiments and calculations, and together with RZ participated in the overall data interpretations and were involved in drafting the manuscript. BD, ZT, RZ and JC revised the manuscript for the intellectual content. All authors read and approved the final version of the manuscript.
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