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Comments on the paper “Influence of ethylenediaminetetraacetic acid on the performance of ferrous sulphate heptahydrate nonlinear optical single crystal”

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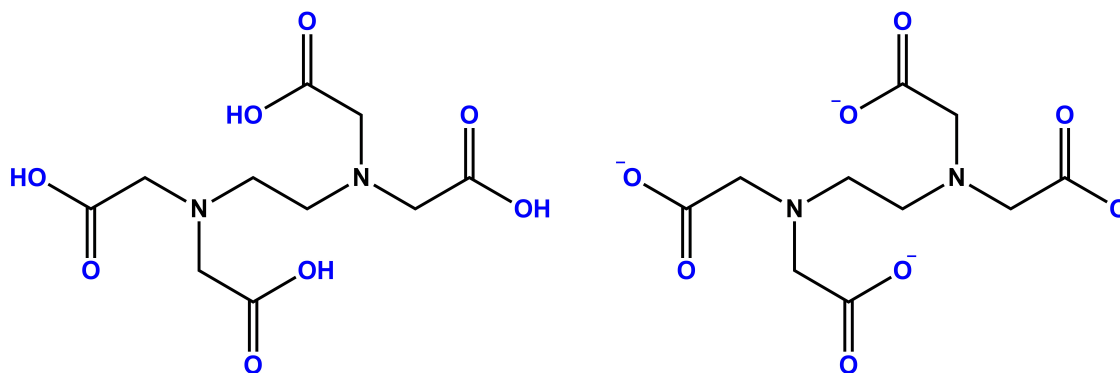
Abstract

The authors of the title paper (Mater. Lett. **161** (2015) 224-226) claimed to have grown ethylenediaminetetraacetic acid doped ferrous sulfate heptahydrate (FeEDTA) crystal by slow evaporation method. In this letter, many points of criticism concerning the growth of the so-called FeEDTA crystal are described to prove that it is in fact surface degraded $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystal.

Keywords: *crystal growth; ferrous sulphate heptahydrate; ethylenediaminetetraacetic acid; crystal structure; optical materials; surface degradation*

Introduction

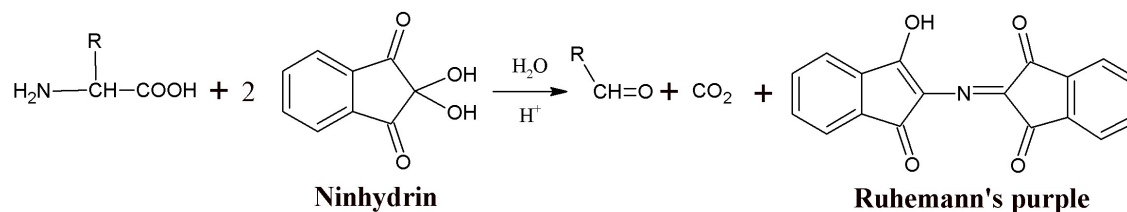
Recently we became aware of the title paper by Pasupathi et al [1] published in Materials Letters reporting on the growth and characterization of a so-called ‘*ethylene diamine tetra acetic acid doped with ferrous sulphate hepta hydrate*’ crystal (**I**)¹ abbreviated by the code FeEDTA. This paper attracted our attention due to the manner in which the well-known reagent ethylenediaminetetraacetic acid ($\text{H}_4\text{-EDTA}$) (Scheme 1) was written in the title and the rest of the manuscript and the claim “*Its diamagnetic nature was confirmed by vibration spectrum magnetometer technique*” in the abstract. A perusal of the title paper revealed several scientific inconsistencies, which are described in this letter to the Editor.



Scheme 1 – Structure of H₄-EDTA (left) and (EDTA)⁴⁻ tetraanion (right). Acidic protons are shown in blue

A so-called ethylenediaminetetraacetic acid doped with ferrous sulfate heptahydrate (I) is in fact a surface degraded FeSO₄·7H₂O

From the experimental procedure it is seen that **I** was grown by slow evaporation of an aqueous solution containing FeSO₄·7H₂O and H₄-EDTA taken in 0.98:0.02 mole ratio. The solubility of H₄-EDTA (formula weight 292.24) is 0.5 g/L [2]. Hence it is surprising that this reagent was used for crystal growth in water. The molecular formula of **I** cannot be seen anywhere in the paper despite the claim of having characterized it by single crystal method. The only information about its chemical composition is that **I** contains 146 μg of H₄-EDTA per ml. This composition was supposedly determined based on a colorimetric estimation of H₄-EDTA in **I** using ninhydrin as the colour-forming reagent. Authors reported, “*Ninhydrin was added with our sample because it is having the capacity to bind with amino acids and imparts stable color (pale yellowish green).*” However, they did not consider that only α-amino acids containing an amino group (-NH₂) react with ninhydrin to give a characteristic purple coloured product known as Ruhemann’s purple (Scheme 2) [3, 4]. Since H₄-EDTA does not contain any -NH₂ group (See Scheme 1) the reported claim of its determination in **I** by the ninhydrin method is inappropriate. Indeed, the reported characterization details provide no evidence whatsoever for the presence of H₄-EDTA, as described below.



Scheme 2. Reaction of α -amino acids with ninhydrin. For mechanism see [4].

In their discussion of diffraction data authors reported “*From the single crystal XRD analysis it was observed that the grown crystals possess monoclinic structure with the lattice parameter values $a=14.077\text{\AA}$; $b=6.509\text{\AA}$; $c=11.054\text{\AA}$; $\alpha=\gamma=90^\circ$ and $\beta=105.16^\circ$ and they were compared with that of the parent material. From that it is perceived that the dopant does not alter the crystal system.*” Although, no reference was given, based on unit cell data one can make out that the parent material is ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) which crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [5]. Hence one does not understand why **I** is called a nonlinear optical crystal. It is not clear if the unit cell from a powder pattern (for example $a=14.06739\text{\AA}$) can be determined to an accuracy of 0.00001\AA .

Although it is not clear what is meant by “*Vibration Spectrum Magnetometer plot of FeEDTA crystal*” in the legend of the UV–Vis–NIR spectrum of **I** (Fig S1) a band gap of 2.733 eV (454 nm) was reported. However, no absorption is observed in the entire visible region showing that this claim is incorrect. It is noted that the magnetic property of **I** was studied using a vibrating sample magnetometer (VSM). In the discussion authors reported, “*VSM result exhibits paramagnetic behavior*”. Contradicting this, it is mentioned in the abstract and conclusion that **I** is diamagnetic. A scrutiny of the magnetic field versus magnetic moment graph reveals that the profile is that of a paramagnetic material. However, the graph shows surprisingly high value of magnetic moment than expected for paramagnetic $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. This can be explained due to magnetic oxide impurity formed by surface degradation of **I**. An

examination of the grown crystals indeed reveals the presence of iron(III) oxide impurities in the form of yellowish brown colour on the surface (Fig S2). A slow surficial oxidation of Fe^{+2} had occurred during its growth from an unacidified ferrous sulphate solution. The presence of oxide impurities can probably explain the unexpectedly high magnetic moment value as well as the observed second harmonic generation (SHG) response of **I** since the centrosymmetric $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ cannot give any SHG response.

The authors described the structure of **I** as a hexacoordinated iron compound (Fig S2) bonded to a tetra-anionic hexadentate ligand. However, this structure is inappropriate due to the following reasons. The crystal growth reaction is supposed to have been performed in 0.98:0.02 mole ratio of Fe(II) reagent and $\text{H}_4\text{-EDTA}$ (so-called dopant) but not in equimolar ratio. The structure in Fig. S2 indicates the presence of a tetra-anionic EDTA (Scheme 1) and for charge balance there should be additional cations. The structurally characterized Fe(III) and Fe(II) compounds of tetra-anionic EDTA [6, 7] contain a seven coordinated central metal due to the presence of a terminal aqua ligand and a hexadentate $(\text{EDTA})^{-4}$ and the Fe(II) compound is crystallized under inert conditions [7]. The absence of any $\text{H}_4\text{-EDTA}$ in **I** is also confirmed by the unit cell data which is in good agreement with that of ferrous sulphate heptahydrate. The structure of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ consisting of two crystallographically unique $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ cations located on inversion centres, a crystallographically independent sulfate anion and a lattice water molecule rules out any incorporation of anionic EDTA ligand as the central metal is coordinatively saturated (Fig 1).

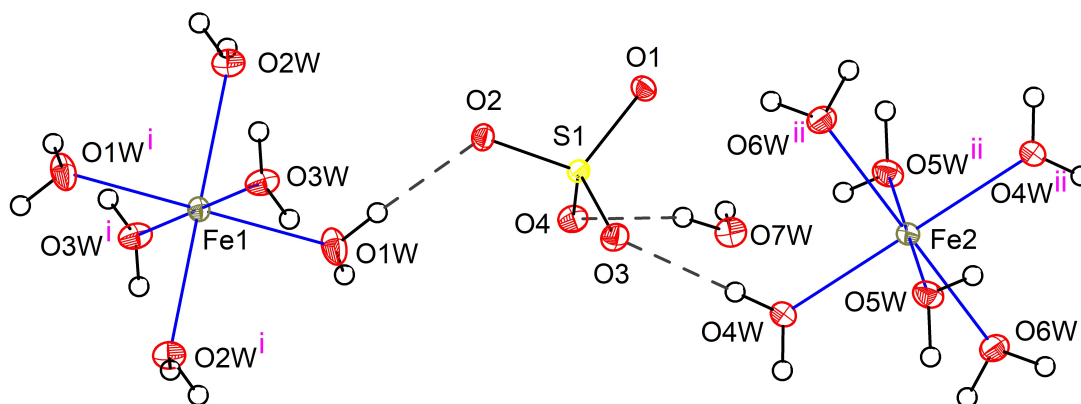
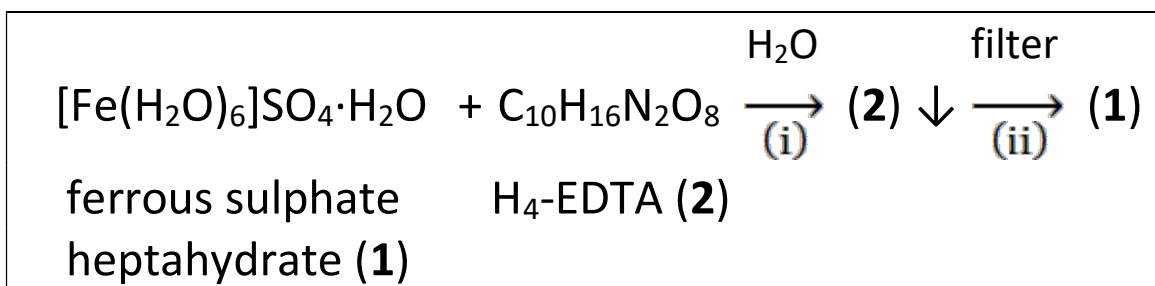


Fig. 1 Crystal structure of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ showing the atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level for all non-hydrogen atoms. Intramolecular H-bonding is shown by broken lines. Symmetry code: i) $-x, 1-y, 1-z$ ii) $1-x, 1-y, -z$. Figure drawn using the CIF file reported in [5]

In order to verify the exact nature of **I**, the crystal growth reaction was reinvestigated by slow evaporation of an aqueous solution containing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{H}_4\text{-EDTA}$ (Scheme 3) in 0.98:0.02 mole ratio. From this two-step reaction, the less soluble $\text{H}_4\text{-EDTA}$ could be recovered in near quantitative yield confirming its fractional crystallization. Its non-incorporation in the crystal structure of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is not surprising since $\text{H}_4\text{-EDTA}$ does not get deprotonated to bind with Fe(II) , under the reaction conditions. Filtration of $\text{H}_4\text{-EDTA}$, followed by slow evaporation of the filtrate acidified with H_2SO_4 as reported in [8] afforded pure $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.



Scheme 3 Reinvestigation of crystal growth of **(I)**. (i) dissolution in water; (ii) filtration.

The foregoing discussions prove unambiguously that a so-called ethylenediaminetetraacetic acid doped with ferrous sulfate heptahydrate (FeEDTA) crystal **I** is in fact a surface degraded $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystal.

Conclusion

In summary, many doubts arise from a reading of the title paper, starting from the purpose of the study. There are many mistakes concerning basic chemistry concepts for example the ninhydrin test. Many cited references are not relevant for the study.

Declaration of Competing Interest: None

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Footnote¹ compound is referred to as **I** to avoid use of a long name

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Supplementary material for ONLINE

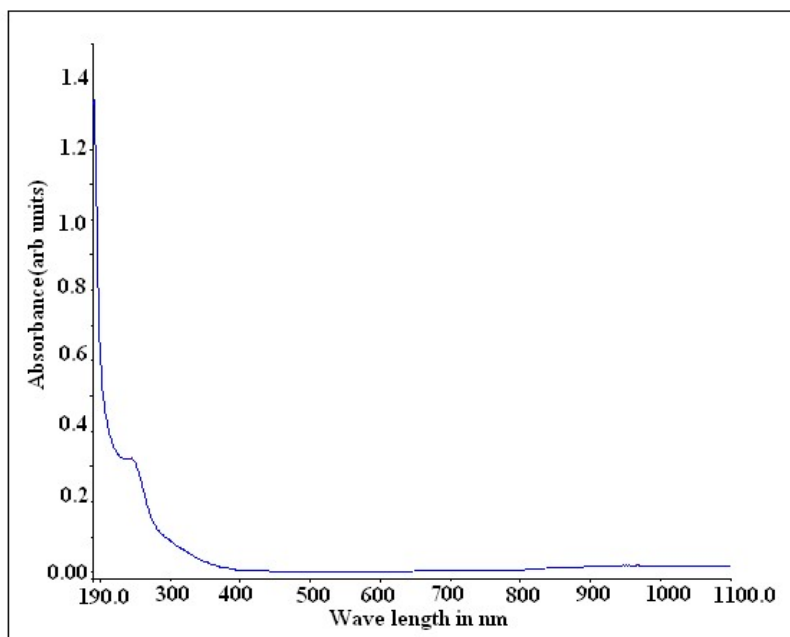


Fig S1 Vibration Spectrum Magnetometer plot of FeEDTA crystal (Note this is Fig 3 in title paper). Reproduced with permission

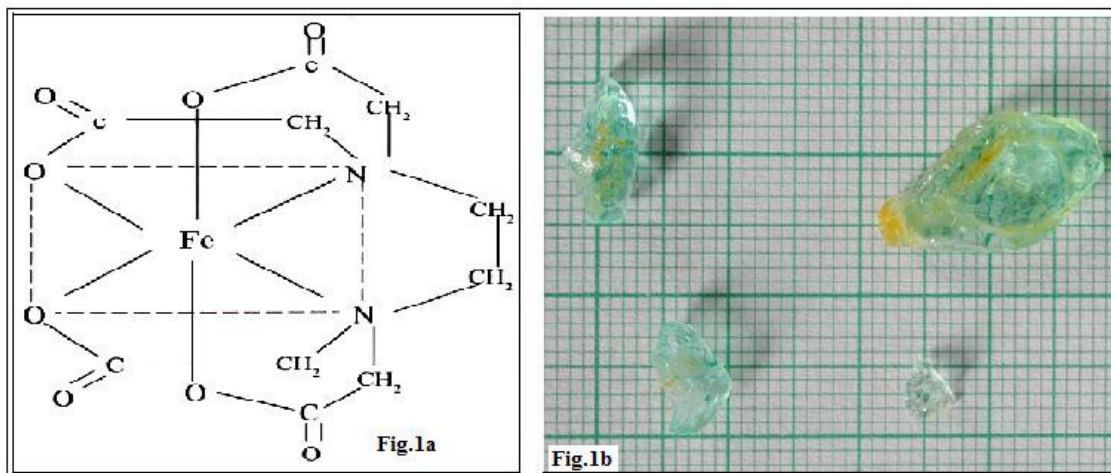


Fig S2 -- Structure of FeEDTA and as grown FeEDTA crystal (This Fig 1a and 1b in the title paper). Note the patches of yellow prominently visible in the crystals in the top row (left). The structure indicates binding of Fe to a tetraanionic EDTA. Reproduced with permission.