The presence of other anions, as impurities and/or doping agents, may alter crystallization and the properties of the crystal. The objective of this research is to examine the effect of thiocyanate doping in the synthesis of cobalt oxalate crystals grown in silica gel. The synthesis was conducted at room temperature for 12 weeks in a U-tube glass filled with silica gel. The gel was prepared from Na$_2$SiO$_3$ at pH 5 using dilute HNO$_3$ with a gelling time of 5 days. Supernatant solutions of (NH$_4$)$_2$C$_2$O$_4$ and Co(NO$_3$)$_2$/KSCN were added on each side of the tube. The Co(NO$_3$)$_2$ and KSCN were firstly mixed before adding onto the gel to increase the possibility of thiocyanate doping in the crystals. Various molar ratio of Co(II):C$_2$O$_4$$^2$-:SCN$^-$ were used (1:1:0, 1:1:1, 1:1:2, 1:1:3, 1:1:4, and 1:1:5). FT-IR and SEM were used to analyse the crystal. The result shows that red block crystals were formed. FTIR analysis for all molar ratios reveals that they all give considerably identical spectra with an absence of thiocyanate peaks around 2200 cm$^{-1}$, suggesting that all molar ratios give an identical product of cobalt(II) oxalate hydrate. SEM analysis shows that the size of the crystals was significantly bigger than previously reported crystals. The Co(II) centre binds to the oxalate ligand, and not to the thiocyanate, due to chelating effect. However, inconclusive findings were observed regarding the influence of the molar ratio on the crystals yield. The use of a higher concentration of thiocyanate (fivefold molar ratio) did not affect the composition of the product, and the product remains crystallized as cobalt(II) oxalate hydrate.

1. Introduction
Cobalt oxalate crystal is commonly used as magnetic materials [1]. The crystal may be used as a precursor in the synthesis of multipurpose Co$_3$O$_4$ nanoparticles [2]. Due to its electronic properties, the cobalt(II) oxalate can be used as a molecule-based magnet or single-chain magnet. Oxalate ions as building blocks have versatile coordination mode, which allows two metal ions connected by the oxalate bridge. Electronic and magnetic properties of cobalt(II)-oxalate is predicted to be influenced by introducing π electron donor ligand, such as thiocyanate (SCN).

Due to the very low solubility of cobalt(II) oxalate in water, which is 2.68 × 10$^{-9}$ [3], the compound is directly precipitated as amorphous powder. Thus, it is difficult to introduce thiocyanate into cobalt(II) oxalate complex by directly mixing the oxalate and Co(II) solutions. A 1D polymeric structure of [Co(H$_2$O)$_2$(C$_3$O$_4$)$_6$ (Figure 1) was reported previously in which the oxalate acts as bridging ligands between two Co metal ions [4,5].
Figure 1. Polymeric structure of cobalt(II) oxalate hydrate (blue = cobalt(II), black = carbon, red = oxygen, white = hydrogen).

Silica gel as a growth medium of metal complexes possesses fascinating features in the synthesis of a low soluble compound due to its ability in controlling crystals nucleation by lowering the diffusion rate of ions [6]. The stability of Si–O–Si networks in the gel also provide space for crystal nuclei to grow into bigger and better single crystals [6]. Previously, we have studied the growth of lead(II) oxalate hydrate [7] and cobalt(II) oxalate crystals in silica gel [8]. The results show that although the crystallisation took in months, U-tube technique gave bigger and better crystal shape than the single-tube technique. Meanwhile, in the case of cobalt(II) oxalate hydrate by in the single-tube technique, direct precipitation or crystallisation of the product may be postponed by the use of different solvents, such as methanol, ethanol, or acetonitrile. In addition, both U-tube and single-tube techniques gave an identical product of cobalt(II) oxalate hydrate.

The work reported here is aiming to examine the effect of thiocyanate doping in the synthesis of cobalt(II) oxalate crystals grown in silica gel using U-tube technique. As frequently reported that the presence of other anions, as impurities, doping agents and/or metal salts, may influence the reaction equilibrium, and thus alter the crystallization and the properties of the crystals [9-11].

2. Materials and Methods

2.1. Materials and Measurements

All chemicals (Merck) were used as received without further purification, namely cobalt(II) nitrate hexahydrate, potassium thiocyanate, nitric acid, sodium oxalate, and sodium silicate. Crystals obtained from all molar ratio were analysed by Fourier Transform–Infrared Spectrophotometry (FTIR-8601PC) in Brawijaya University – Malang (using KBr pellet method in the range of 4000 – 400 cm⁻¹) and Scanning Electron Microscope (FEI Inspect S50) in State University of Malang - Indonesia.

2.2. Preparation of Gel and Supernatant Solutions

Silica gel was prepared from mixing Na₂SiO₃ 0.5 M to 100 mL HNO₃ 1 M until pH 5. A 30 mL of the solution was then transferred in a U-tube transparent glass (inner diameter = ± 2.5 cm) and stand at room temperature for 5 days until the gel is formed. Meanwhile, the supernatant solutions, solution A and B, were prepared in 1:1 ratio. Solution A was prepared by diluting 200 mg Co(NO₃)₂·6H₂O (0.687 mmol) in 20 mL of water, while solution B was prepared by diluting 92.1 mg Na₂C₂O₄ (0.687 mmol) in 20 mL of water. The molar ratio of Co²⁺:C₂O₄²⁻: SCN⁻ were varied (1:1:0; 1:1:1; 1:1:2; 1:1:3; 1:1:4; and 1:1:5). For ratios of 1:1:1 to 1:1:5, the solution A was also added with KSCN (66.8 mg; 133.6 mg; 200.4 mg; 267.2 mg; and 334.0 mg, respectively).

2.3. Crystal Growing

After the gel was ready, solution A and solution B were added separately on each side of the U-tube (Figure 2). Two sets of reactions were prepared for every molar ratio. After that, the tubes were closed with aluminium foil and the reactions were stood at room temperature for 12 weeks. Isolation of the
crystals was done by firstly remove both solutions, then hot water was added to dissolve the gel and finally filtered off. The crystals were dried in an oven (50-60 °C) for 3 hours and save it in a desiccator.

Figure 2. Illustration of gel-growth cobalt(II) oxalate crystals.

3. Result and Discussion

3.1. Crystal Growing
In week 6, several tiny single crystals started to form in the gel in every molar ratio, in which the area where crystal grew was approximately in between the two solution pathways or in the middle of the gel, as shown in Figure 3. The crystals grew bigger in the following weeks and red block single crystals were yielded by the end of week 12. Theoretically, the growth time can be shortened by increasing the concentration of both solutions.

The average yield of the obtained crystals is given in Table 1. Based on physical examination under the microscope, crystals obtained from all molar ratios have identical colour (red-orange) and morphology, indicating the uniformity of the compound in bulk product. The crystal yields were varied from 40 to 100 mg regardless of the molar ratio. At this stage, the inconclusive correlation between the thiocyanate concentrations and the crystal yields is noted. The isolation technique that was used to separate the crystal from the gel may influence the yield since the crystals were considerably tiny and fragile.

Figure 3. Crystal (dark spots) growing in silica gel, taken from the ratio of 1:1:5.

| Table 1. The average yield of the obtained crystals for each molar ratio. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ratio | 1:1:0 | 1:1:1 | 1:1:2 | 1:1:3 | 1:1:4 | 1:1:5 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Yield (mg) | 90 | 50 | 40 | 70 | 100 | 90 |
3.2. Analyses of the crystal

Crystals obtained from all molar ratios were analysed by FT-IR and SEM. The IR spectra of the crystals from all molar ratios (Figure 4) shows that there is a sharp peak close to 1600 cm$^{-1}$ which corresponds to carbonyl (C=O) stretching vibration, and two identical sharp peaks of the C–O symmetric and asymmetric stretch around 1300 cm$^{-1}$. Furthermore, a sharp peak around 800 cm$^{-1}$ shows O–C–O asymmetric vibration, while a sharp peak around 500 cm$^{-1}$ corresponds to Co–O stretch vibration, as also reported by Wang [2]. In addition, a sharp peak that occurs around 3300 cm$^{-1}$ indicates that there is an O–H vibration of water as hydrate. Details of absorption peaks, wave numbers (cm$^{-1}$) and interpretations of IR spectra for every molar ratio are given in Table 2.

![Figure 4. IR spectra of crystals obtained from all ratios (blue = 1:1:0; black = 1:1:1; violet = 1:1:2; red = 1:1:3; green = 1:1:4; brown= 1:1:5).](image)

| Co(II) : C$_2$O$_4^{2-}$ : SCN$^-$ | Interpretation   | References |
|----------------------------------|------------------|------------|
| 1:1:0                            |                  |            |
| 1:1:1                            |                  |            |
| 1:1:2                            |                  |            |
| 1:1:3                            |                  |            |
| 1:1:4                            |                  |            |
| 1:1:5                            |                  |            |
| 3369                             | $\nu$(O-H)       | [2, 4, 5, 8]|
| 1618                             | $\nu$(C=O)       | [2, 4, 5, 8]|
| 1362                             | $\nu$(C–O) asymmetric | [2, 4, 5, 8]|
| 1317                             | $\nu$(C–O) symmetric | [2, 4, 5, 8]|
| 825                              | $\nu$(O-C-O) asymmetric | [2, 4, 5, 8]|
| 494                              | $\nu$(Co–O)      | [2, 4, 5, 8]|

Initially, the thiocyanate doping was intended to replace the water ligand to alter the magnetic properties of the cobalt(II) complex. Analogue to this is a 1D polymeric complex of oxalate-bridged M(II) (M = Co, Ni, Cu) with aminopyridine ligand [12]. However, crystals obtained from all ratios

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**Table 2. IR spectra of the crystals obtained from all ratios.**

| Co(II) : C$_2$O$_4^{2-}$ : SCN$^-$ | Interpretation   | References |
|----------------------------------|------------------|------------|
| 1:1:0                            |                  |            |
| 1:1:1                            |                  |            |
| 1:1:2                            |                  |            |
| 1:1:3                            |                  |            |
| 1:1:4                            |                  |            |
| 1:1:5                            |                  |            |
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Initially, the thiocyanate doping was intended to replace the water ligand to alter the magnetic properties of the cobalt(II) complex. Analogue to this is a 1D polymeric complex of oxalate-bridged M(II) (M = Co, Ni, Cu) with aminopyridine ligand [12]. However, crystals obtained from all ratios.
shows identical infrared spectra (Figure 4) and confirm the absence of specific bands that correspond to SCN vibration, such as a sharp peak of CN group around 2200 cm\(^{-1}\). If sharp peak around 2200 cm\(^{-1}\) was observed, the presence of SCN in the crystal, either as coordinating ligand to cobalt(II) or as counter ions of the complex in the crystal lattice is confirmed. Therefore, it is concluded that crystals from all molar ratios were in fact a complex of cobalt(II) oxalate hydrate as reported previously by our group [7,8] and others [2,4,5,13]. Although the thiocyanate was firstly mixed with the cobalt(II) solution to increase the possibility of producing thiocyanate-cobalt(II) complex, the doping (until molar ratio of 1:1:5) was not affecting the final product and the oxalate ions remains having high preference to bind to the Co(II) centre than to the thiocyanate ions due to chelating effect. Higher thiocyanate concentration (up to ten-fold of the oxalate) might be needed to increase the possibility of introducing the ion into the cobalt(II) complex successfully.

Since all molar ratio gave identical product, the SEM analysis was conducted only to one crystal, which is from the ratio of 1:1:5. SEM image of the crystals is presented in Figure 5. The crystals have long block morphology and red-orange colour, in which the size is significantly bigger than that of identical crystals reported by Wang et al. [2], Bacsa et al. [4], and Bowen et al. [13]. The SEM image (mag = 400 ×) also gives more evidence that the use of silica gel as growth media, especially using the U-tube method, can lead to a bigger and better single crystal of insoluble salts or metal complexes.

![SEM image of crystal at Co(II):oxalate:SCN ratio of 1:1:5.](image)

**Figure 5.** SEM image of crystal at Co(II):oxalate:SCN ratio of 1:1:5.

For further research, the use of a higher concentration of thiocyanate or different anion should be investigated. Other variables, such as pH of gel, type of cobalt(II) salts and/or solvents also need to be considered. Other techniques for introducing thiocyanate ions into the complex, such as solvothermal, might also need to be explored.

4. Conclusion
Various molar ratio of \(\text{Co}^{2+}:\text{C}_2\text{O}_4^{2-}:\text{SCN}^-\) (1:1:0 to 1:1:5) gives identical red-orange block crystals of cobalt(II) oxalate hydrate. Although the thiocyanate ions were not successfully doped into the crystals or influence the final product, bigger crystals were obtained by using this U-tube gel technique. In the final product, the oxalate ions remain to have a high preference to bind to the Co(II) centre than to the thiocyanate ions due to chelating effect.

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