

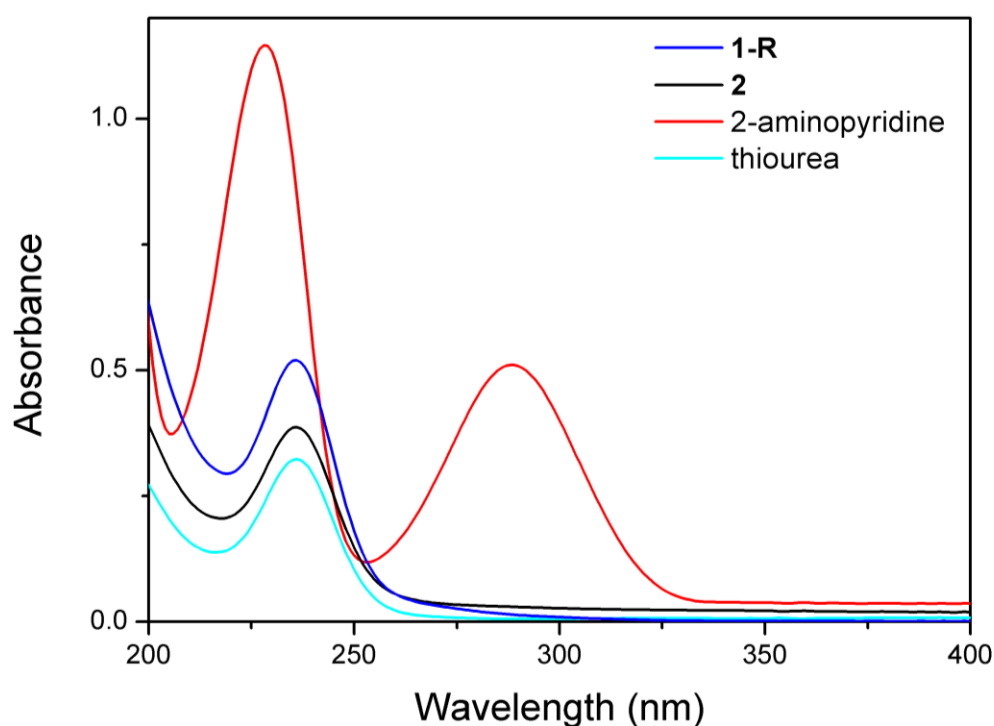
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## Reinvestigation of growth of 2-aminopyridine bis thiourea zinc sulphate single crystal

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### Graphical abstract

Reinvestigation of the growth of 2-aminopyridine bis thiourea zinc sulphate crystal **1** reported earlier (J. Mol. Struc. 1048, (2013) 238-243) reveals that **1** is actually the well-known compound sulphatotris(thiourea)zinc(II) **2**.



### Highlights

Growth of 2-aminopyridine bis thiourea zinc sulphate crystal (**1**) is reinvestigated.

We prove (**1**) is actually sulphatotris(thiourea)zinc(II).

UV-Vis spectra prove the absence of 2-aminopyridine in the grown crystal.

## Reinvestigation of growth of 2-aminopyridine bis thiourea zinc sulphate single crystal

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### Abstract

In an earlier published paper, Srineevasan and Rajasekaran (J. Mol. Struc. 1048, (2013) 238-243) [1] reported to have grown a so called 2-aminopyridine bis thiourea zinc sulphate single crystal (1) by slow evaporation technique at room temperature. A reinvestigation of the reported crystal growth reaction reveals that addition of 2-aminopyridine into an aqueous solution containing zinc sulphate heptahydrate and thiourea in 1:2 mole ratio initially results in the formation of a white precipitate. Filtration of the precipitate followed by slow evaporation of the filtrate results in the crystallization of the known compound sulphatotris(thiourea)zinc(II) (2) and NOT any 2-aminopyridine bis thiourea zinc sulphate.

**Keywords:** 2-aminopyridine; thiourea; 2-aminopyridine bis thiourea zinc sulphate; sulphatotris(thiourea)zinc(II); dubious crystal

## Introduction

During a survey of the literature of zinc-thiourea compounds, we came across a paper reporting on the growth and optical studies of 2-aminopyridine bis thiourea zinc sulphate single crystals [1]. In view of our interest on the growth of thiourea based crystals of zinc [2, 3] this paper attracted our attention. Although a mention of single crystal study was made in the abstract, no molecular formula was reported for the so called 2-aminopyridine bis thiourea zinc sulphate **1**. Instead the title crystal was identified by a five letter code viz. 2-APTZS **1**<sup>1</sup>. A perusal of the paper revealed that the authors have reported only the orthorhombic unit cell parameters and the cell volume of **1**. The authors of [1] compared the unit cell volume of **1** (818 Å<sup>3</sup>) with the cell volume (1354 Å<sup>3</sup>) of a known compound sulphatotris(thiourea)zinc(II) formulated as [Zn(tu)<sub>3</sub>(SO<sub>4</sub>)] (tu=thiourea) **2** [4].

Compound **2** is well documented in the literature since its crystal structure was first determined under the name tris(thiourea) zinc sulphate in 1968 [5]. In this paper, we have used the IUPAC name sulphatotris(thiourea)zinc(II) for a zinc(II) compound containing three monodentate thiourea ligands and a monodentate sulphate ligand [6]. Zinc tris(thiourea) sulphate (abbreviated as ZTS) is another name used in crystal growth literature [7-11] for **2**. Based on a comparison of the cell volumes of **1** and **2**, the authors reported, “*Lesser cell volume of 2-APTZS (1) with ZTS (2) indicates that the 2-aminopyridine ions entered into the ZTS crystal lattice*”. However the above explanation is quite unreasonable for a very large reduction of more than 500 Å<sup>3</sup> in unit cell volume. The incorporation of a 2-aminopyridine (C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>) ligand containing seven non-hydrogen atoms in place of a thiourea ligand (CH<sub>4</sub>N<sub>2</sub>S) in **2** containing only four non-hydrogen atoms is actually expected to result in an enhanced cell volume. In spite of this, the authors claimed that a reduction cell volume resulted in coordination of the pyridine N to the central metal in **1** and proposed a structure

showing that Zn(II) is bonded to two terminal thiourea ligands, a monodentate 2-aminopyridine ligand and a monodentate sulphate ligand. In addition to the cell volume inconsistency, it is observed that the spectral characterization of **1** is quite unconvincing. The reported IR spectrum of **1** is very similar to the IR spectrum of **2** with bands indicating the presence of only thiourea and sulphate moieties but no 2-aminopyridine [2]. In the discussion of UV-Vis spectrum authors reported '*peaks around 532 nm confirms pi bond transitions*'. The reported  $^{13}\text{C}$  NMR data did not account for the different C atoms in 2-aminopyridine.

In view of several inconsistencies with respect to unit cell and spectral data, the reported crystal growth reaction of **1** has been reinvestigated in order to characterize the exact nature of the product formed from an aqueous solution containing  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 2-aminopyridine and thiourea in 1:1:2 ratio. The product of the reaction was characterized by infrared (IR), Raman, UV-Visible spectra and X-ray powder pattern. The results of these investigations are described in this paper.

## Experimental

All the chemicals used in this study were of reagent grade and were used as received without any further purification. Double distilled water was used as solvent for all crystal growth studies. Crystals of the known compound sulphatotris(thiourea)zinc(II) (**2**) used as a reference for characterization were prepared as described earlier [6]. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from  $4000\text{--}400\text{ cm}^{-1}$  at a resolution of  $4\text{ cm}^{-1}$ . Raman spectra were recorded using 785 nm laser radiation for excitation with laser power set to 100 mW on an Agiltron PeakSeeker Pro Raman instrument. UV-Visible spectra of aqueous solutions were recorded on a Shimadzu UV-2450 double beam spectrophotometer (200–800 nm) using matched

quartz cells. X-ray powder pattern were recorded on a Rigaku Miniflex II powder diffractometer using Cu-K $\alpha$  radiation with Ni filter.

#### *Reinvestigation of crystal growth of 2-aminopyridine bis thiourea zinc sulphate 1*

An aqueous solution of zinc sulphate heptahydrate (1.006 g, 3.5 mmol) was added into an aqueous solution of thiourea (0.532 g, 7.0 mmol) and the reaction mixture was stirred well resulting in a clear solution. Addition of an aqueous solution of 2-aminopyridine (0.329 g, 3.5 mmol) into the above reaction mixture resulted in an immediate precipitation of small quantities of white compound. The entire reaction mixture was stirred for 4 h and filtered. The white residue was washed well with cold water and dried. The filtrate was left undisturbed for slow evaporation of the solvent. No special efforts were taken to grow large crystals. The crystalline product (**1-R**) thus obtained was washed with small amounts of cold water and air dried. Yield of isolated product was 0.610 g. The label (**1-R**) is given to show that this is the reinvestigated product.

### **Results and discussion**

#### *Synthetic aspects of the crystal growth of 1-R*

In this work we have reinvestigated the growth of a so called 2-aminopyridine bis thiourea zinc sulfate crystal **1** to address the inconsistencies in its earlier characterization [1] and to correctly identify the exact product. For the crystal growth of **1** no details of the amounts of reagents used and the yield of the crystalline product were reported. Instead the resistivity of Millipore water used was given. For our reinvestigation, the crystal growth reactions were performed on a gram scale (3.5 mmol) of ZnSO<sub>4</sub>·7H<sub>2</sub>O. All three reagents namely zinc sulphate heptahydrate, thiourea and 2-aminopyridine are water soluble and were used in 1:2:1 mole ratio as described in the earlier work. Addition of aqueous 2-aminopyridine into an aqueous solution containing the other two reactants resulted in the immediate precipitation of

a white compound presumably zinc hydroxide. The formation of this precipitate which was not mentioned in [1] can be explained due to the basic nature of 2-aminopyridine. The insoluble nature as well as an IR spectrum which shows absence of characteristic bands of the organic moieties viz. thiourea and 2-aminopyridine adds credence to the formation of hydroxide. Filtration of the precipitate followed by slow evaporation of the filtrate afforded a crystalline material which is referred to as compound **1-R**. For the characterization of the crystals grown in this study, the powder pattern, infrared, Raman and optical spectra of **1-R** and **2** were recorded and the results of these studies are described below.

#### *Discussion of Spectral characteristics*

For a closed shell  $d^{10}$  metal ion like zinc(II) the electronic transitions are expected to be ligand centered and not metal centered. A comparison of the UV-Visible spectra of thiourea, 2-aminopyridine, compounds **1-R** and the reported compound sulphatotris(thiourea)zinc(II) **2** proves the absence of any 2-aminopyridine whatsoever in **1-R** (Fig. 1). Unlike thiourea which exhibits a single band ( $\lambda_{\max} = 236$  nm) 2-aminopyridine exhibits two charge transfer bands at 228 nm and 288 nm respectively. The optical spectra of thiourea and **2** are identical and exhibit a single broad band centered at 236 nm which can be attributed to the intra ligand charge transfer of thiourea. In both cases the chromophore responsible for UV absorption is thiourea. Interestingly, the UV-Vis spectrum of **1-R** matches perfectly with the spectrum of thiourea, but does not match with the spectrum of 2-aminopyridine. Thus a comparative study of the UV-Vis spectra of the free ligands and the Zn(II) compounds **1-R** and **2** serve to demonstrate the absence of the 2-aminopyridine chromophore in **1-R**. For compound **1** the authors of [1] had reported the cut off wavelength as 265 nm which is also in accordance with the absence of 2-aminopyridine.

The IR and Raman spectra of **1-R** are identical with those of the reported compound sulphatotris(thiourea)zinc(II) **2** (Fig. 2) indicating that both compounds **1-R** and **2** are one and the same. In order to confirm this unambiguously, a few more batches of crystals of **1-R** were checked and in all cases the spectra were always the same as that of **2**. This clearly indicates that no so called 2-aminopyridine bis(thiourea) zinc sulfate crystal is formed. Since compound **2** has been extensively studied in the literature [6–11] and vibrational spectroscopy is used as a characterization tool to infer if a new product is formed, no discussions of the spectra and the assignment of bands are presented here. In order to unambiguously confirm that **1-R** is the known compound sulphatotris(thiourea)zinc(II) (**2**) the powder pattern of both compounds (Fig. 3) were compared, which reveals both phases are one the same. In view of the absence of 2-aminopyridine in **1-R** and the identical nature of the infrared and Raman spectra and powder pattern, we find no need to determine the crystal structure for any further characterization of **1-R**.

The above discussed results unambiguously rule out the reported claim of replacement of a thiourea ligand in **2** by 2-aminopyridine. The formation of a tris(thiourea) compound **2** instead of a bis(thiourea) compound **1** indicates that in the presence of sulphate anions Zn(II) prefers to bind to a minimum of three thiourea ligands and does not prefer to bind to a N-donor ligand like 2-aminopyridine. In an earlier report [2] we have shown that an attempted incorporation of urea to grow crystals of a so called thiourea urea zinc sulphate from an aqueous solution containing thiourea, urea and ZnSO<sub>4</sub> in 1:1:1 mole ratio failed and the only crystal that could be isolated was compound **2**. Hence the formation of a tris(thiourea) compound is along expected lines as described below.

Based on phase rule investigations of the zinc sulphate / thiourea / water system at 30°C it has been shown that only a tris(thiourea) compound of composition [Zn(tu)<sub>3</sub>(SO<sub>4</sub>)] **2**

(tu=thiourea) is formed between zinc sulfate and thiourea [6]. In this context it is interesting to note that bis(thiourea) [12-14] and tetra(thiourea) [15] compounds of zinc are well documented in the literature for chloride, acetate and nitrate anions, in the case of sulphate only the tris(thiourea) compound **2** is known. The low product yield also explains the formation of a tris(thiourea) compound and not any bis(thiourea) compound of zinc as assumed by the authors of [1]. In view of our synthetic results we are quite surprised at the reported unit cell data of **1**, which is quite different from that of **2**. It is not clear if the unit cell was actually measured or an altogether different compound was used for unit cell determination or the measurement was erroneous. Due to the non-reporting of a CIF file for single crystal structure determination and the absence of accompanying refinement details like space group, molecular formula, absorption coefficient,  $\theta$  range for data collection, reflections collected, refinement method etc. we are of the opinion that the reported unit cell is quite unreliable.

From the foregoing discussions it is quite obvious that the reinvestigated crystal **1-R** is actually the well known compound sulphatotris(thiourea)zinc(II) **2**. For the improper characterization of a so called 2-aminopyridine bis thiourea zinc sulphate **1**, the explanation we wish to offer is that the formulation of **1** was not performed based on an analysis of experimental data but was done based on an incorrect assumption namely slow evaporation of an aqueous solution containing  $\text{ZnSO}_4$ , thiourea and 2-aminopyridine in 1:2:1 mole ratio will result in the formation of **1**. In view of an improper characterization other investigations like dielectric studies and NLO studies are meaningless and hence are not discussed.

## Conclusions

The reinvestigation of the crystal growth of a so called 2-aminopyridine bis thiourea zinc sulphate single crystal **1** sets the literature right by proving the earlier report to be completely



erroneous. We hope that the present results will encourage authors to characterize new compounds based on a complete single crystal structure determination.

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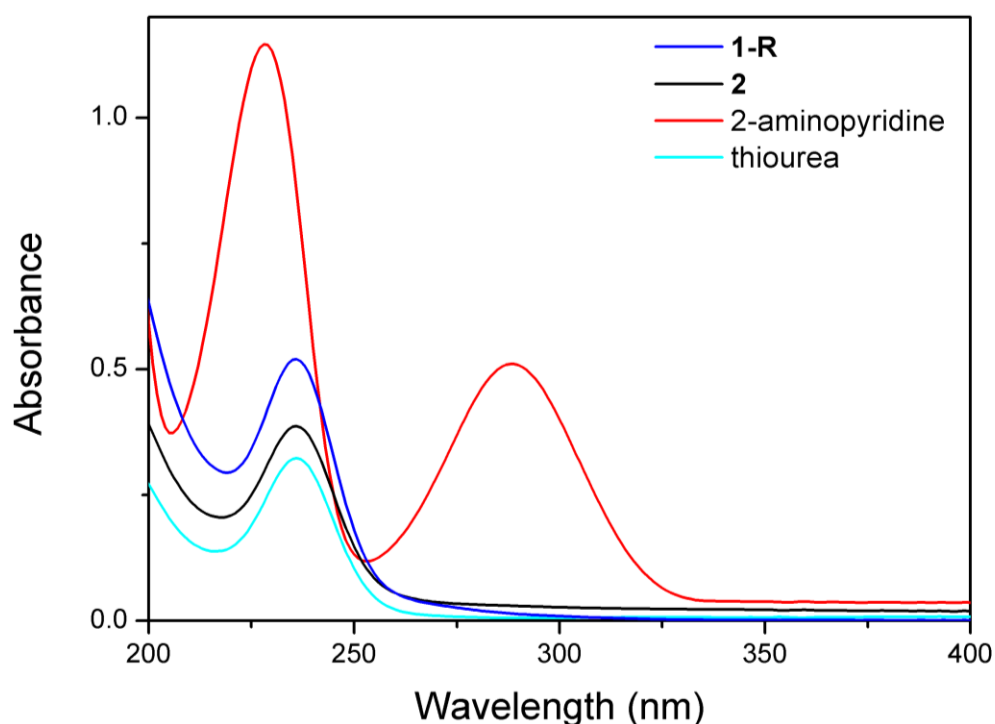
## Footnote

<sup>1</sup> To avoid use of a long code the title crystal is referred to as compound **1** in this manuscript.

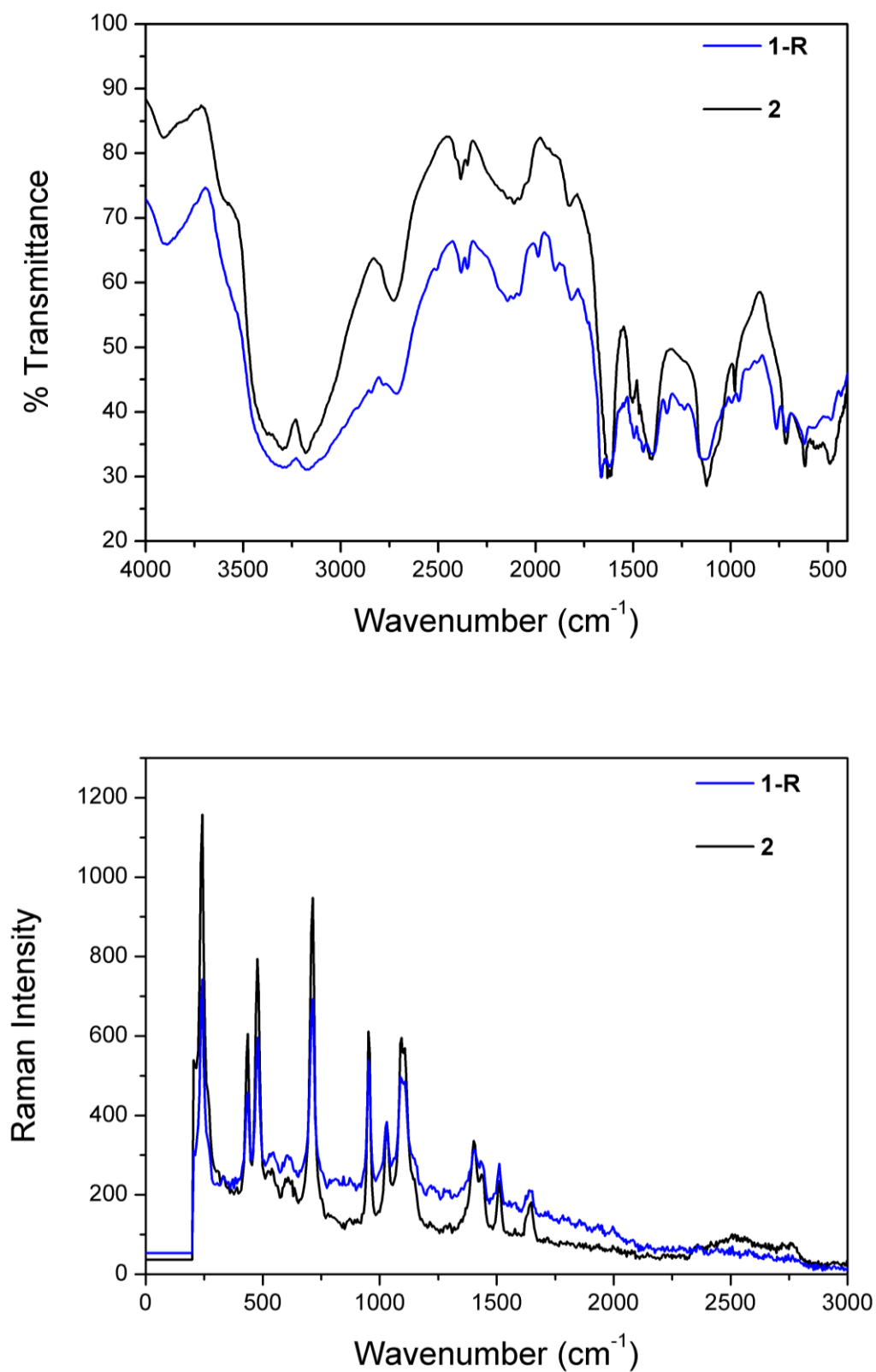
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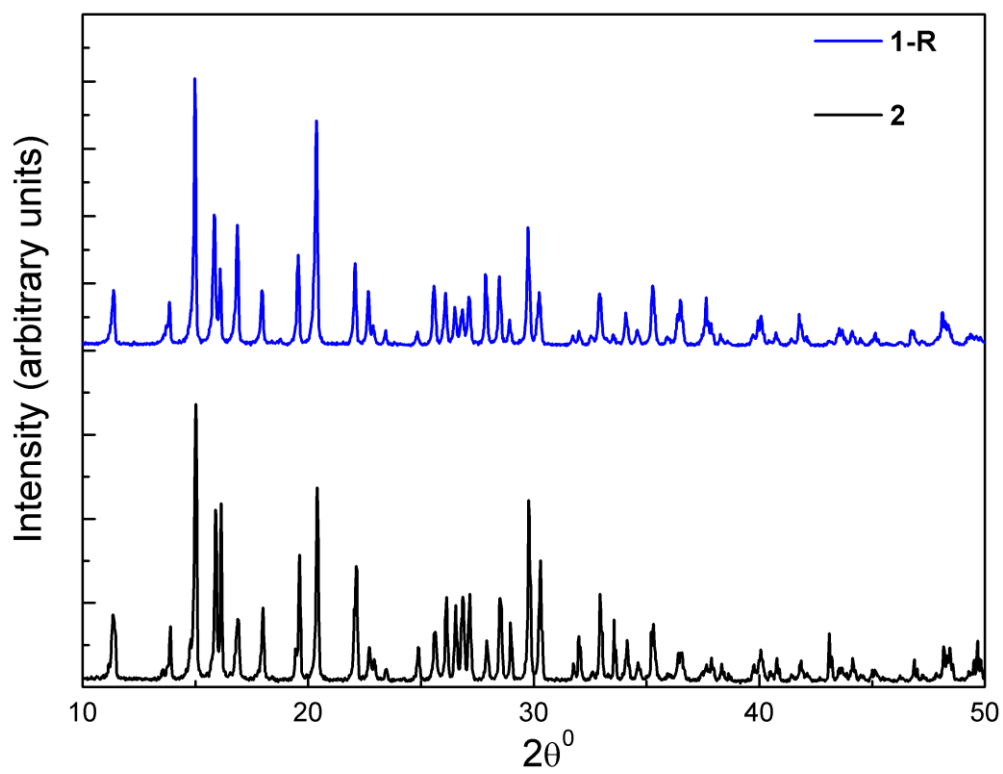
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**Fig . 1** UV-Vis spectra of aqueous solutions of **1-R**, **2**, 2-aminopyridine and thiourea.



**Fig. 2.** Infrared (top) and Raman spectra (bottom) of **1-R** and **2**.



**Fig. 3** X-ray powder pattern of **1-R** (top) and **2** (bottom).