

# On the crystal growth of ‘tris thiourea chromium(III) sulphate’, ‘potassium thiourea thiocyanide’ and ‘bis thiourea iron(II) sulphate’

Bikshandarkoil R. Srinivasan<sup>1</sup> · Zbigniew Tylczyński<sup>2</sup>

Received: 29 May 2015 / Accepted: 9 June 2015 / Published online: 21 July 2015  
© The Author(s) 2015. This article is published with open access at Springerlink.com

**Abstract** We argue that the ‘tris thiourea chromium(III) sulphate’ crystal (Madhurambal et al. in J Therm Anal Calorim 108:905–910, 2012), potassium thiourea thiocyanide crystal (Ramamurthi et al. in J Therm Anal Calorim 104:943–947, 2011) and bis thiourea iron(II) sulphate crystal (Madhurambal et al. in J Therm Anal Calorim 108:911–914, 2012) are actually thiourea.

**Keywords** Tris thiourea chromium(III) sulphate · Bis thiourea iron(II) sulphate · Potassium thiourea thiocyanide · Thiourea · Dubious crystal

## Comment

During a survey of the literature of metal–thiourea compounds, we came across papers claiming growth and characterization of so-called tris thiourea chromium(III) sulphate **1** [1], potassium thiourea thiocyanide **2** [2] and bis thiourea iron(II) sulphate **3** [3] crystals. For these crystals that were claimed as novel nonlinear optical (NLO) materials, the authors did not report any molecular formula but instead unusual codes, for example, TTCS for tris thiourea chromium(III) sulphate. To avoid use of such nonstandard codes, compounds are referred to by numbers in this comment. In recent papers, we have highlighted on

the importance of reporting the molecular formula for new compounds [4–6]. In this letter, we show the usefulness as well as limitations of unit cell data for characterization of new compounds, using the title compounds as examples.

The authors of the papers on the title compounds have formulated their compounds based on an incorrect assumption that the reaction of a metal salt (e.g. chromium sulphate) with thiourea will result in the formation of their expected crystal (e.g. **1**) and not based on an analysis of the unit cell, infrared (IR) and optical spectra and thermal analytical data. This can be evidenced by several of their claims some of which are quoted for **1**. ‘The characteristic vibrational frequency of pure thiourea and TTCS (compound **1**) are very similar. However for heavily doped chromium(III) sulfate some vibrational changes have been noticed in the FTIR spectrum. The heavily doped Cr(III) spectrum indicates some distortion lattice as a result of Cr(III) into the tris thiourea crystalline matrix. This is because of the formation of TTCS complex, decreases the bond length of C=S and hence larger energy required for this transition, and hence absorption shows the blue end of the spectrum’. It is not clear what the authors mean by heavily doped chromium(III) sulphate. Cr(III) compounds are known to be coloured, but the reported optical spectrum of **1** clearly indicates that it is a colourless solid. The authors claim to have characterized **1** with the aid of unit cell data, but a comparison of the reported cell (Table 1) with that of the unit cell of thiourea [7] unambiguously reveals that **1** is nothing but pure thiourea.

The above result is not surprising because the reaction of chromium(III) sulphate with thiourea in 1:3 urea leads to the fractional crystallization of the less soluble thiourea and not any tris(thiourea) complex as assumed by the authors of [1]. It is well known that Cr(III) compounds are substitution inert and no structurally characterized Cr(III)–thiourea compound is reported in the Cambridge Database till date.

✉ Zbigniew Tylczyński  
zbigtyl@amu.edu.pl

Bikshandarkoil R. Srinivasan  
srini@unigoa.ac.in

<sup>1</sup> Department of Chemistry, Goa University, Goa 403206, India

<sup>2</sup> Faculty of Physics, Adam Mickiewicz University,  
Umultowska 85, 61-614 Poznan, Poland

**Table 1** Comparative unit cell data

Compound	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$	Space group	Volume/ $\text{Å}^3$	Ref.
Pure thiourea	5.488(3)	7.663(4)	8.564(4)	<i>Pbnm</i>	360.1	[7]
So-called tris thiourea chromium sulphate <sup>a</sup> <b>1</b>	5.4881 <sup>b</sup>	7.6620 <sup>b</sup>	8.5495 <sup>b</sup>	–	359.5	[1]
So-called potassium thiourea thiocyanide <sup>a</sup> <b>2</b>	5.4891 <sup>b</sup>	7.6560 <sup>b</sup>	8.5505 <sup>b</sup>	$P2_12_12_1$ <sup>c</sup>	359.3	[2]

<sup>a</sup> No CIF data for structure determination

<sup>b</sup> No ESD values given

<sup>c</sup> Incorrect space group

The reported unit cell data for compound **2** once again confirm that the crystal formed is thiourea and not any so-called potassium thiourea thiocyanide. Although it is not clear as to how the authors could report a  $P2_12_12_1$  space group for **2**, the absence of any CIF data for structure refinement indicates the dubious nature of the space group claim. The formation of thiourea as the product can be explained due to the fractional crystallization of the less soluble thiourea with the more soluble potassium thiocyanate (incorrectly called as potassium thiocyanide by the authors) remaining in solution. This result is in agreement with the known chemistry of K which is a known oxophilic metal. In accordance with the formation of thiourea, the reported infrared spectra of **1** and **2** perfectly match with the IR spectrum of pure thiourea. A similar proof based on IR spectrum has been recently used to show that the so-called thiourea urea magnesium chloride and urea thiourea sodium chloride are actually thiourea [4]. For compound **3**, the authors did not report any unit cell data. However, a comparison of the IR spectrum with that of the spectra of **1** and **2** confirms that **3** is also thiourea. The reported UV–Vis spectra and thermal curves of **1–3** are also identical providing additional evidence that the compound under study is thiourea. Since the unit cell, IR and UV–Vis spectra and thermal data prove that no new compound other than thiourea is formed, we do not wish to comment on the other results, for example, the dielectric data. The title compounds described in this letter once again highlight the importance of reporting molecular formula for any new crystalline material and reporting single crystal data substantiated by structure refinement and not just unit cell data.

## Conclusions

We have shown that the so-called tris thiourea chromium(III) sulphate **1**, potassium thiourea thiocyanide **2** and bis thiourea iron(II) sulphate crystal **3** are all dubious crystals.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

## References

1. Madhurambal G, Ravindran B, Mariappan M, Mojumdar SC. Growth and characterization of tris thiourea chromium(III) sulphate. *J Therm Anal Calorim.* 2012;108:905–10.
2. Ramamurthy K, Madhurambal G, Ravindran B, Mariappan M, Mojumdar SC. The growth and characterization of a metal organic crystal, potassium thiourea thiocyanide. *J Therm Anal Calorim.* 2011;104:943–4.
3. Madhurambal G, Ravindran B, Mariappan M, Mojumdar SC. Investigation on the growth and characterization of nonlinear optical single crystal of bis thiourea iron(II) sulphate. *J Therm Anal Calorim.* 2012;108:911–4.
4. Srinivasan BR. On the existence of ‘thiourea urea magnesium chloride’ and ‘urea thiourea sodium chloride’. *J Therm Anal Calorim.* 2015;119:985–8.
5. Srinivasan BR, Natarajan S, Gururaja G, et al. Comments on the papers recently published by Sangeetha et al. *J Therm Anal Calorim.* 2015;120:1071–5.
6. Srinivasan BR, Tylczyński Z. Comments on the paper “Growth and characterization of semi-organic nonlinear optical crystal: urea thiourea cadmium sulfate”. *J Therm Anal Calorim.* 2015. doi:10.1007/s10973-015-4636-7.
7. Takahashi I, Onodera A, Shiozaki Y. Structural changes of thiourea in connection with its phase transitions: reappraisal of rigidity and libration of the molecule. *Acta Crystallogr.* 1990; B46:661–4. doi:10.1107/S0108768190006012.