Published in **Optik**, 127, (2016) 2500-2501 http://dx.doi.org/10.1016/j.ijleo.2015.11.169

Once again on the existence of "1,3 diglycinyl thiourea"

Aram M. Petrosyan[a], Bikshandarkoil R. Srinivasan[b]

[a] Institute of Applied Problems of Physics, NAS of Armenia, 25 Nersessyan Str., 0014 Yerevan, Armenia. Email:apetros@iapp.sci.am
[b]Department of Chemistry, Goa University, Goa 403206, India. Email: srini@unigoa.ac.in

Abstract

We argue that the existence of the compound "1,3 diglycinyl thiourea" reported by Kumar et al (Optik 126, 1117–1122 (2015)) and two more previous publications is not confirmed by structure determination to date and the title compound is a dubious crystal.

Keywords: *1,3 diglycinyl thiourea, improper characterization, α-glycine*

Introduction

Publications of erroneous articles may not only lead to their subsequent correction, but also to the emergence of new erroneous publications. As examples of the latter, the publications on "bis-glycine sodium nitrate", "glycine picrate", "*L*-threonine formate" (see [1-4] and references therein) and the tile crystal can be pointed out. In the scientific literature the confusion on a so-called "1,3 diglycinyl thiourea" was first introduced by Ezhil Vizhi and Kalainathan [5] and later continued by Sabari Girisun and Dhanuskodi [6]. Very recently a paper by Kumar et al also devoted to "1,3 diglycinyl thiourea" has appeared [7]. In the following comment we show that "1,3 diglycinyl thiourea" reported in three papers so far [5-7] is a dubious crystal.

Comment

A so-called "1,3 diglycinyl thiourea" crystal was claimed to have been crystallized for the first time from an aqueous solution containing glycine and thiourea in 2:1 molar ratio [5]. The authors assumed that the following reaction (equation 1) with elimination of water molecules is possible in aqueous solution.

$$2(NH_3CH_2COO) + SC(NH_2)_2 \rightarrow NH_2\text{-}CH_2\text{-}CO\text{-}NH\text{-}CS\text{-}NH\text{-}CO\text{-}CH_2\text{-}NH_2 + 2\ H_2O \quad .. (1)$$

It is not clear why the authors chose an inappropriate name 1,3 diglycinyl thiourea for the above formula instead of the correct name *N,N'*-thiocarbonylbis(2-aminoacetamide). In addition to a dubious name, the authors claimed "*The structure of the grown crystal was solved by single crystal XRD analysis by direct method and retired* (probably should be '*refined*') *by the full matrix-least-squares*

technique using SHELXL program". However, no structure was determined and only unit cell parameters without space group were reported. The authors of [5] reported also the infrared spectrum and thermal curves of the grown crystal, which as was indicated in [8] perfectly match with respective data of α-form of glycine [9] and prove that the so called "1,3 diglycinyl thiourea" crystal actually is the centrosymmetric α-form of glycine (see Table 1 for unit cell parameters). The authors of [5] also reported that the "1,3 diglycinyl thiourea" crystal displays 2.6 times greater second harmonic generation output power than in potassium dihydrogenphosphate (KDP), which is impossible because of the centrosymmetric nature of the α-glycine crystal. The authors of [6] also have claimed to have obtained crystals of "1,3 diglycinyl thiourea" according to [5] and identified by unit cell parameters determined from powder XRD pattern (see Table 1). The authors of [6] also reported SHG signals 2.5 times greater than in KDP which once again is impossible considering the agreement of the unit cell data with α-glycine [9].

The authors of [7] claim to have obtained the compound "1,3 diglycinyl thiourea" according to conditions described in [5]. The authors of [7] identified the grown crystal as "1,3 diglycinyl thiourea" by unit cell parameters determined from powder XRD pattern shown in Table 1, which in their opinion are in good agreement with data reported in [5].

Table 1. Crystallographic data of α-form of glycine and "1,3 diglycinyl thiourea"

Unit cell data	α-glycine	So called "1,3 diglycinyl thiourea"		
a	5.1054(6)	5.091	5.113(2)	5.5753
b	11.9688(19)	11.980	11.988(4)	5.994
c	5.4645(9)	5.45	5.564(3)	12.273
β	111.697(11)	111.92	112	113
V	310.25	309.12		310.81
Z	4	-	-	-
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	-	-	-
Reference	[9]	[5]	[6]	[7]

In this paper, the structure and spectroscopic data of the "1,3 diglycinyl thiourea" molecule is supposed to have been calculated by *ab initio* Hartree-Fock and density functional theory methods. The authors of [7] claim that calculated data are compared with experimental data. Optimized geometric parameters are compared with "experimental X-ray data / ref. [11]", where C. Kemnitz, Chemoffice Ultra 10. Trial Version, 2002" is cited as reference "[11]". The authors of [7] provided "experimental" infrared spectrum of "1,3 diglycinyl thiourea", which neither corresponds to theoretical spectrum nor to the spectrum of α-form of glycine. The strongest four absorption bands of "experimental" spectrum in 3000-2000 cm^{-1} range are absent in the table of wavenumbers of

absorption peaks and assignment. The authors of [7] have shown also powder XRD indexed pattern, which is questionable. In the reported pattern there are two peaks with the same 020 and three peaks with 200 hkl indices at different angles. In our opinion all these indicate on dubious nature of this most recent work on a so called "1,3 diglycinyl thiourea".

Conclusions

To date the structure of the "1,3 diglycinyl thiourea" crystal has not been determined. The unit cell parameters, the infrared spectrum and the thermal curves of "1,3 diglycinyl thiourea" obtained in [5] coincide with that of α-form of glycine. The authors of [6, 7] obtained crystals at the conditions described in [5] and identified as "1,3 diglycinyl thiourea", which indicates on dubious nature of these papers. We do hope that based on our critical comments on the results of the published papers on 1,3 diglycinyl thiourea [5-7], these or other authors will be able to obtain under appropriate conditions, a genuine 1,3 diglycinyl thiourea namely *N*,*N'*-thiocarbonylbis(2-aminoacetamide), if it really exists.

References

[1] A.M. Petrosyan, Comment on the paper by R. Sankar, C.M. Ragahvan, R. Mohan Kumar, R. Jayavel, "Growth and characterization of bis-glycine sodium nitrate (BGSN), a novel semiorganic nonlinear optical crystal", J. Crystal Growth 309(2007) 30-36. J. Crystal Growth 310, 3810-3811 (2008).

[2] A.M. Petrosyan,"Comment on "Growth and characterization of glycine picrate single crystal" by T. Uma Devi et al., Spectrochim. Acta A71(2008) 340-343". Spectrochim. Acta A 75, 1176 (2010).

[3] V.V. Ghazaryan, M. Fleck, A.M. Petrosyan, Glycine glycinium picrate –Reinvestigation of the structure and vibrational spectra. Spectrochim. Acta A 78, 128-132 (2011).

[4] A.M. Petrosyan,V.V. Ghazaryan, M. Fleck, On the existence of "*L*-threonine formate", "*L*-alanine lithium chloride" and "bis *L*-alanine lithium chloride" crystals, Spectrochim. Acta A 105, 623-625 (2013).

[5] R. Ezhil Vizhi, S. Kalainathan, Growth and characterization of a new organic NLO material: 1,3 Diglycinyl thiourea. Mater. Lett. 62, 791-794 (2008).

[6] T.C. Sabari Girisun, S. Dhanuskodi, Nonlinear optical susceptibilities of diglycinyl thiourea for frequency conversion and optical limiting applications. Chem. Phys. Lett. 491, 248-253 (2010).

[7] M. Kumar, R. Kanagadurai, G. Mani, S. Gunasekaran, S. Kumaresan, Synthesis, growth, molecular structure and spectral studies of 1,3 diglycinyl thiourea by density functional method. Optik 126, 1117–1122 (2015).

[8] M. Fleck, A.M. Petrosyan, Difficulties in the growth and characterization of non-linear optical materials: a case study of salts of amino acids. J. Crystal Growth, 312, 2284-2290 (2010).

[9] P.-G. Jönsson, A. Kvick, Precision neutron diffraction structure determination of protein and nucleic acid components. III. The crystal and molecular structure of the amino acid α-glycine, Acta Crystallogr. B28, 1827–1833 (1972).