Published in Spectrochim Acta 163A (2016) 58-59 http://dx.doi.org/10.1016/j.saa.2016.03.013

Comments on "Synthesis aspects, structural, spectroscopic, antimicrobial and room temperature ferromagnetism of zinc iodide complex with Schiff based ligand" by K. Shakila and S. Kalainathan, Spectrochim. Acta 135A (2015) 1059-1065

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Abstract

Shakila and Kalainathan report on the synthetic and structural aspects of a zinc iodide complex with Schiff based ligand, which exhibits room temperature ferromagnetism. In this comment, many points of criticism, concerning the characterization of this so called zinc iodide complex of Schiff based ligand are highlighted to prove that the title paper is completely erroneous.

Keywords: zinc iodide; Schiff base; thiocarbamide; ferromagnetism; room temperature; dubious solid.

Comment

From the title of the commented paper [1], it appears that the authors describe the synthetic aspects, structure and magnetic study of a zinc iodide complex with Schiff based ligand. However, on reading the abstract of the paper it is noted that the work described in the title paper is actually on the growth of a complex compound of zinc iodide with thiocarbamide by slow evaporation method. Since thiocarbamide (also known as thiourea) with formula (H_2N-CS-NH_2) has nothing to do with Schiff base (R_2C=NR'), starting from the title, the paper is questionable. In addition the reported claim of observing room temperature ferromagnetism for their Zn(II) compound has been the subject matter of an interesting Pub Peer discussion [2] showing many claims in the paper are dubious. A scrutiny of the title paper reveals that the authors claim to have grown crystals of a known compound namely bis(thiourea)zinc(II)iodide having formula [$Zn(CH_4N_2S)_2I_2$] (CH_4N_2S is thiourea) previously reported by Albov et al., [3] showing a tetrahedral geometry for Zn(II) (Fig. 1) due to the binding of two monodentate thiourea ligands via S and two iodo ligands.

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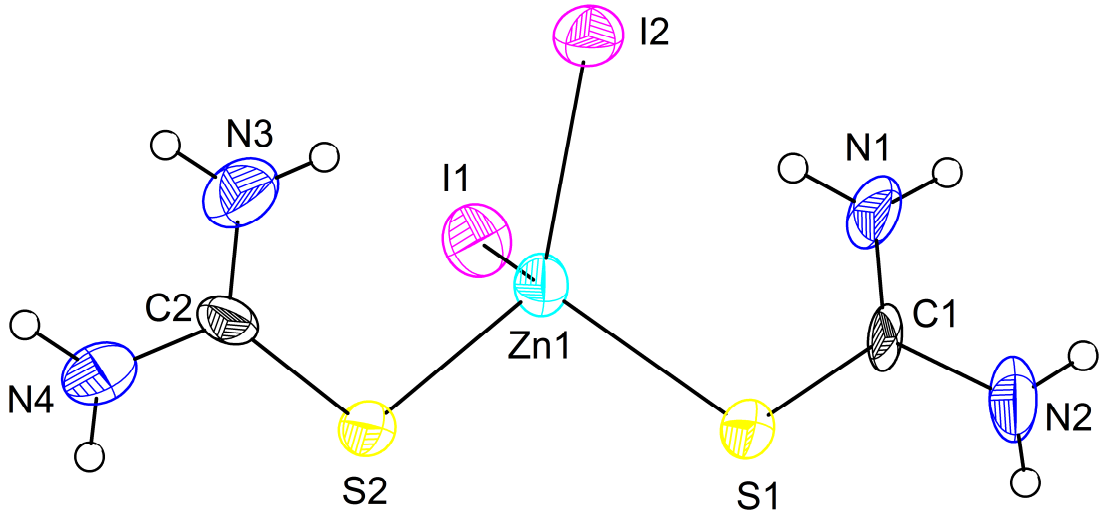

Fig.1 The crystal structure of $[Zn(CH_4N_2S)_2I_2]$ (CH_4N_2S is thiourea) showing a tetrahedral geometry for Zn(II). Displacement ellipsoids are drawn at 50% probability level excepting for H atoms which are shown as circles of arbitrary radii. Note. Figure is drawn using the CIF file reported by Albov et al [3].

It is not clear why the authors wanted to grow crystals of this Zn(II) complex which in their opinion was already a known crystal. Although the authors claimed to have characterized the alleged compound $[Zn(CH_4N_2S)_2I_2]$ by single crystal and powder diffraction, only unit cell parameters and an indexed powder pattern were reported. It is noted that the authors claim in the absence of a CIF file that their unit cell is in agreement with reported data. The X-ray work in the title paper has been criticized by Sylvain Bernes, a former Co-Editor of Acta Crystallographica Section E, who doubts if the authors ever synthesized a pure $[Zn(CH_4N_2S)_2I_2]$ phase [2]. According to Bernes the indexation given in the powder pattern is meaningless since, the reflection (220) is indexed at lower Bragg angle than (001) and he opines that this senseless indexation was due to an improper use of the program TERROR. A comparison of the XRD pattern computed (for details see [4]) using the published single crystal structure of Albov et al., [3] reveals that the expected pattern is completely different from the pattern reported by the authors of the title paper. The mismatch of the reported X-ray powder pattern with the theoretical pattern calculated from the reported structure can be due to any of the following: i) It is possible that the crystal used for powder diffraction was different from the one used by Shakila & Kalainathan for the unit cell data in the single crystal because the authors actually got a mixture of several products. ii) It is also possible that no unit cell was measured but some convenient values close to the reported cell of

Albov et al., were chosen because authors assumed that mixing of thiourea and ZnI_2 will result in their expected product. In this context, it may be noted that another unit cell reported by the same two authors for a so called thiosemicarbazide lead nitrate crystal is on very similar lines and has also shown to be dubious [5].

One finds it strange that authors did not determine the structure with the single crystal study; instead they claim to have performed an EDAX experiment for the determination of the elemental composition based on which they make a remarkable claim, '*EDAX data confirms the presence of zinc iodide in TZI crystal and also confirms the absence of impurities*'. In a recent report Srinivasan and Narvekar [6] have shown that EDAX is an inappropriate method for characterization of new materials based on elemental composition data. The spectral discussion reporting "*N–C–S bending vibration is observed at 569 cm−1 confirms the formation of metal–sulphur coordination bond*" can only be termed very unfortunate.

In view of the above mentioned discussions especially a questionable powder pattern it appears no genuine phase of $[Zn(CH_4N_2S)_2I_2]$ was actually synthesized by this group for any study including unit cell determination. Hence all claims including magnetic studies in the paper are meaningless. As pointed out recently [7] claims of ferromagnetic behavior for the closed shell (d^{10}) zinc(II) (or cadmium (II)) compounds based on very weak magnetic signals is due to the inexperience of the authors to correctly interpret magnetic data. The observation of room temperature ferromagnetism for a diamagnetic compound unambiguously confirms the dubious nature of the title crystal. The foregoing discussions prove that contrary to the authors' claim, the title crystal is not a new example of a ferromagnetic zinc(II) compound; It is actually a dubious crystal.

The main result of the title paper [1] is the publication by K. Shakila and S. Kalainathan in a peer reviewed international Journal with an Impact Factor of 2.206 (for 2014). The scientific content of the title paper does not really matter because there is hardly any.

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[3] D.V. Albov, E.A. Buravlev, E.V. Savinkina, I.A. Zamilastkov, Synthesis and structure of zinc iodide complex with thiocarbamide, $[Zn(CH_4N_2S)_2I_2]$ Crystallography Reports, 58 (2013) 65–67. http://dx.doi.org/10.1134/S1063774513010033

[4] For details of comparison of X-ray powder pattern see http://i.imgur.com/ShtC81H.jpg?

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[7] B.R. Srinivasan, M.Z. Naik, K.U. Narvekar, Comment on “Synthesis, growth and characterization of a new metal–organic NLO material: Dibromo bis (*L*-proline) Cd(II) ” [J. Mol. Struct. 1080 (2015) 37–43], J. Mol. Struc. 1099 (2015) 16-17. http://dx.doi.org/10.1016/j.molstruc.2015.06.042