

# Thallium I phenylsuccinic acid coordination polymer as precursor for preparation of thallium (III) oxide nanostructures by direct thermal decomposition

MOHAMMAD JAAFAR SOLTANIAN FARD\*, SARA TABAROKI

Departement of Chemistry, Firoozabad Branch, Islamic Azad University, Firoozabad, Fars, Iran P.O. Box 74715-117

A new thallium (I) coordination polymer  $[Tl(PsucH)]_n$  ( $PsucH$  = phenylsuccinic acid) has been synthesized and characterized by single crystal X-Ray analysis, elemental analysis and IR spectroscopy. The single crystal X-Ray analysis shows that this polymer is 2-D along a axis. Flower-like nanostructure thallium (III) oxide,  $Tl_2O_3$  has been prepared by direct thermal decomposition of thallium (I) coordination polymer. The nanostructure was characterized by scanning electron microscopy (SEM), X-Ray powder diffraction (XRD) and IR spectroscopy. The thermal stability of the  $Tl_2O_3$  nanostructure was studied by thermal gravimetric analysis and differential thermal analysis (TGA /DTA) too.

Keywords: *thallium (I); coordination polymer; nanostructure; thallium (III) oxide*

© Wroclaw University of Technology.

## 1. Introduction

Coordination polymers represent an important interface between synthetic chemistry and material science. There has been recently considerable interest in the design and synthesis of coordination polymers for their novel structural architectures and favorable properties of ion exchange, adsorption, nonlinear optics and magnetism [1–14]. However, there still remain many problems to overcome before the synthesis of coordination polymers with a desired topology is possible. Many parameters are involved in the formation of the metal-organic framework (MOF), such as the metal and its different coordination spheres, the influence of the counter-anion, the metal/ligand ratio, the flexibility and nature of the organic building blocks, the number and orientation of the coordinating sites in the ligands, and the solvent of recrystallization [15–20]. Thallium as a heavy element of group 13 has two oxidation states of +1 and +3. The number of  $Tl^I$  supramolecular polymers which has been reported for this metal ion is significantly lower than for other metal ions.  $Tl^I$  fa-

vors to form neutral species with anionic ligands. Thallium (I) usually favors to form  $Tl \dots Tl$ ,  $Tl \dots C$ ,  $Tl \dots H$  secondary interactions especially on its vacant coordination sphere with stereo-chemically active lone pair which indicates that thallium (I) ion reflects the capacity to act as both a Lewis acid and a Lewis base [21–23]. In this paper we describe one of thallium (I) coordination polymers, thallium (I) phenylsuccinic acid  $[Tl(PsucH)]_n$  and its use for preparation of  $Tl_2O_3$  nanostructure. Thallium (III) oxide is a highly conductive and degenerate n-type semiconductor which may have a potential use in solar cells. A method of producing  $Tl_2O_3$  by MOCVD is known. The powder was characterized by means of powder X-Ray diffraction (XRD), scanning electron microscopy (SEM), IR spectroscopy, thermal gravimetry analysis and differential thermal analysis (TGA and DTA).

## 2. Experimental section

### 2.1. Materials and physical techniques

All reagents and solvents for the synthesis and analysis were commercially available and used as received. IR spectra were recorded using Perkin-

\*E-mail: mohammadjaafar\_soltanian@yahoo.com

Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid apparatus and are uncorrected. Melting points were measured on an Electrothermal 9100 apparatus. X-Ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Phillips company with monochromatized  $\text{CuK}\alpha$  radiation. The crystallite size of selected samples was estimated using the Sherrer formula. Crystallographic measurements were made at 100(2) K using a Bruker APex II Kappa CCD area detector. The intensity data were collected using graphite monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Accurate unit cell parameters and the orientation matrix were obtained from least squares refinement. Intensities were integrated from several series of exposures measured every  $0.5^\circ$  in  $\omega$  or  $\phi$  using the Apex II. Absorption corrections were based on equivalent reflections using SADABS [24], and structures were refined against all  $\text{Fo}^2$  data with hydrogen atoms (on carbon and oxygen atoms) riding in calculated positions using SHELXL [25]. The molecular structure plots were prepared using ORTEP and Mercury [26]. Crystallographic data and details of the data collection and structure refinements are listed in Table 1. The observed anisotropic thermal parameters, the calculated structure factors, and full lists of bond distances, bond angles and torsion angles are given in the supplementary material. TGA and DTA curves were recorded using PL-STA 1500 device manufactured by Thermal Science in a static atmosphere of nitrogen. The nano-oxide with gold coating was characterized with a scanning electron microscope (SEM) (Philips XL 30).

## 2.2. Synthesis of $[\text{Tl}(\text{PsucH})]_n$

The compound  $[\text{Tl}(\text{PsucH})]_n$  was prepared as follows: 1 mmol of phenylsuccinic acid was dissolved in 10 ml methanol and was mixed and stirred with a solution of 1 mmol (0.057 g) KOH in 5 ml  $\text{H}_2\text{O}$ . Then a solution of 1 mmol  $\text{TlNO}_3$  in 5 ml  $\text{H}_2\text{O}$  was added to the mixture and was refluxed for 3 h. After filtering, it was allowed to evaporate for several days and then suitable white crystals were obtained: Melting point  $240^\circ\text{C}$ ,

Anal. Found: C, 30.28; H, 2.21; O, 16.14. Calc. for  $\text{C}_{10}\text{H}_9\text{O}_4\text{Tl}$ : C, 30.21; H, 2.28; O, 16.09%. IR ( $\text{cm}^{-1}$ ) selected bands: 535 m, 640 m, 850 m, 1166 m, 1285 vs, 1529 m, 2221 w and 3203 vs.

## 2.3. Preparation of thallium (III) oxide nanostructure

The  $[\text{Tl}(\text{PsucH})]_n$  was calcined at  $600^\circ\text{C}$  under air atmosphere. The whole organic component was combusted and the thallium (III) oxide nanostructure was produced.

## 3. Results and discussion

Reaction of phenylsuccinic acid ligand with thallium (I) nitrate provided a single crystal of  $[\text{Tl}(\text{PsucH})]_n$ . The single crystal structure shows that this compound in the solid state is a 2-D polymer along a-axis and crystallizes in the monoclinic space group  $P 2_1/c$  respectively (Table 1).

The deprotonated carboxylate group on the ligand acts as both chelating and bridging group so that O2 bridges to two thallium atoms, while O1 bridges to one thallium atom. The O4 atom of deprotonated carboxylic acid acts as a bridging group between 3 thallium atoms. There is only one thallium atom with coordination number 8 and bond distance between  $2.74 - 3.26 \text{ \AA}$ . It seems that the  $6s^2$  lone pair electron of thallium is inactive in this polymer. There is no secondary interaction of  $\text{Tl} \dots \text{Tl}$ ,  $\text{Tl} \dots \text{H}$  and  $\text{Tl} \dots \text{C}$  in the structure too (Figs. 1 and 2).

Nanostructure of  $\text{Tl}_2\text{O}_3$  has been generated by thermal decomposition of  $[\text{Tl}(\text{PsucH})]_n$ . The final product upon calcination of  $[\text{Tl}(\text{PsucH})]_n$  at  $600^\circ\text{C}$ , identified based on its IR, XRD patterns, TGA and DTA analysis, is  $\text{Tl}_2\text{O}_3$ .

Fig. 3 shows an X-Ray powder diffraction pattern of  $\text{Tl}_2\text{O}_3$  nano-structure after calcination of  $[\text{Tl}(\text{PsucH})]_n$  compound. The XRD pattern of  $\text{Tl}_2\text{O}_3$  nanostructure after calcination is almost the same, and it is in a good agreement with a typical structure of  $\text{Tl}_2\text{O}_3$  diffraction pattern (JCPDS No.33-1404). The diffraction peaks shown in Fig. 3 accord with the cubic crystal system with the space group of  $P 2_1/c$  and lattice parameters of

Table 1. Crystal data and structure refinement for [Tl(PsucH)]<sub>n</sub>.

Identification code	A	
Empirical formula	C <sub>10</sub> H <sub>9</sub> O <sub>4</sub> Tl	
Formula weight	397.54	
Temperature	291(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2(1)/ <i>c</i>	
Unit cell dimensions	<i>a</i> = 15.6680(12) Å	$\alpha = 90^\circ$ .
<i>b</i> = 6.7680(11) Å	$\beta = 96.207(9)^\circ$	
<i>c</i> = 9.8850(16) Å	$\gamma = 90^\circ$	
Volume	1042.1(3) Å <sup>3</sup>	
<i>Z</i>	4	
Density (calculated)	2.534 Mg/m <sup>3</sup>	
Absorption coefficient	15.489 mm <sup>-1</sup>	
<i>F</i> (000)	728	
Crystal size	0.22 × 0.11 × 0.09 mm <sup>3</sup>	
Theta range for data collection	2.62 to 25.50°.	
Index ranges	−18 ≤ <i>h</i> ≤ 18, −7 ≤ <i>k</i> ≤ 8, −11 ≤ <i>l</i> ≤ 10	
Reflections collected	4516	
Independent reflections	1802 [ <i>R</i> (int) = 0.1108]	
Completeness to theta = 25.50°	93.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3371 and 0.1323	
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Data / restraints / parameters	1802 / 0 / 112	
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.023	
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0905, <i>wR</i> 2 = 0.2266	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1148, <i>wR</i> 2 = 0.2479	
Largest diff. peak and hole	5.504 and −4.248 e <sup>-3</sup>	

*a* = 10.5700 Å and *Z* = 16. There is no unknown peak in the XRD pattern, what means that no impurities were detected. Sharp diffraction peaks indicate good crystallinity of Tl<sub>2</sub>O<sub>3</sub> nanostructure prepared from the [Tl(PsucH)]<sub>n</sub> compound. The broadening of the peaks indicates that the particles were of nanometer scale. The average grain size *D* has been estimated from the Scherer formula:

$$D = 0.891\lambda / \beta \cos \theta \quad (1)$$

where  $\lambda$  is the X-Ray wavelength (0.17889 nm), and  $\theta$  and  $\beta$  are the diffraction angle and full-

width at half maximum of an observed peak, respectively [27, 28]. Upon the main peak, the average size of the particles in the sample was calculated to be 95 nm, which is in agreement with that observed from the SEM image (Fig. 4).

It shows that the amount of crystalline phase in the final product is very high. Thermogravimetric analysis and differential thermal analysis (TGA/DTA) were carried out to show that the product after calcination of [Tl(PsucH)]<sub>n</sub> did not contain any impurities. There is no noticeable loss of weight in the TGA curve that would prove the ex-

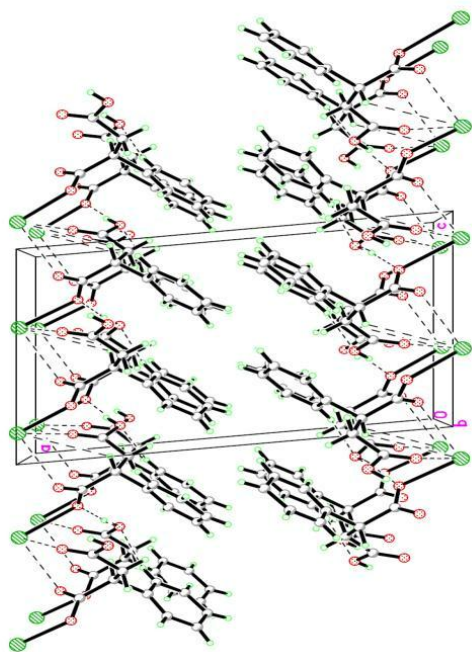


Fig. 1. Crystal packing for  $[Tl(PsucH)]_n$ .

istence of thallium (III) oxide which does not decompose in this temperature range. The broad peak at DTA may be due to inaccuracy of the measuring instrument (Fig. 5).

## 4. Conclusion

One thallium (I) coordination polymer  $[Tl(PsucH)]_n$  was synthesized and characterized by single crystal X-Ray analysis, elemental analysis and IR spectroscopy. We have successfully synthesized nanocrystalline  $Tl_2O_3$  nanoparticles through calcination of a new Tl(I) coordination polymer. As it was previously mentioned the synthesis of nano  $Tl_2O_3$  is not possible by usual method such as sonochemical and hydrothermal and here we have shown that coordination polymer could be a very good precursor for synthesis of nanothallium (III) oxide and we hope nanometal oxide particles with different shapes, obtained from different polymer precursors.

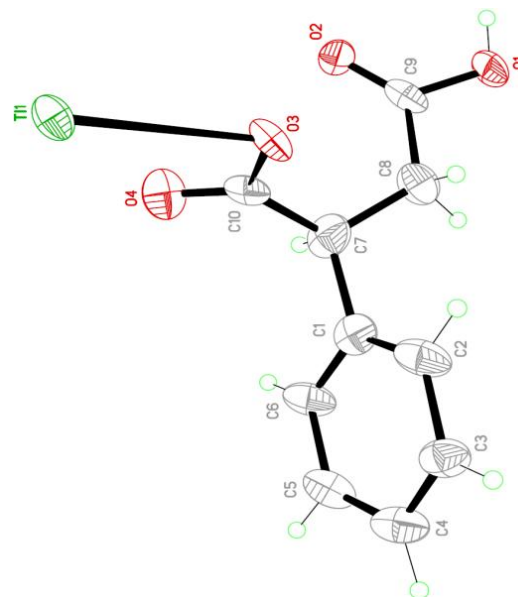


Fig. 2. ORTEP representation of the molecular structures of  $[Tl(PsucH)]_n$ . Thermal ellipsoids are drawn at the 50 % probability level.

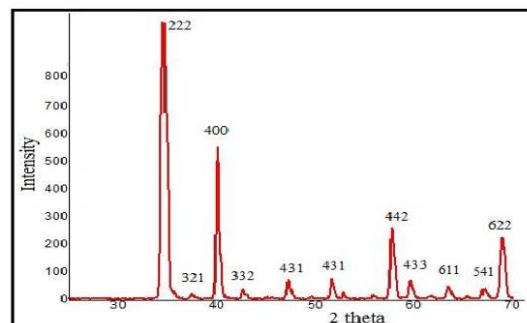


Fig. 3. The XRD pattern of  $Tl_2O_3$  produced by calcination of  $[Tl(PsucH)]_n$ .

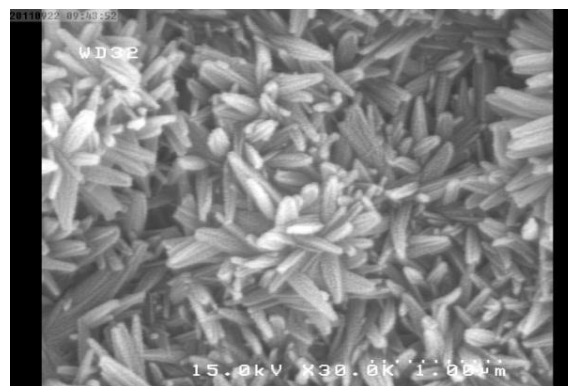


Fig. 4. The SEM image of  $Tl_2O_3$  nanoparticles produced by calcination of  $[Tl(PsucH)]_n$ .

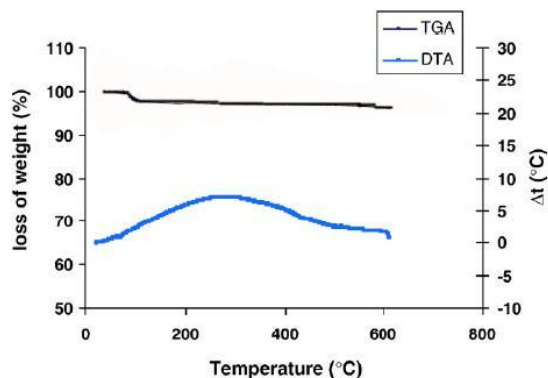


Fig. 5. TGA-DTA curves of  $\text{Tl}_2\text{O}_3$  nano-structure produced by calcinations of  $[\text{Tl}(\text{PsucH})]_n$ .

## 5. Supplementary material

Complete bond lengths and angles, coordinates and displacement parameters have been deposited at Cambridge Crystallography Data Center. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 850743 for compound **1**.

## Acknowledgements

Support of this investigation by Islamic Azad University of Firoozabad is gratefully acknowledged.

## References

- [1] STUMPF H.O., OUAHAB L., PEI Y. GRANDJEAN D., KAHN O., *Science*, 261 (1993), 447.
- [2] GARDNER G.B., VENKATARAMAN D., MOORE J. S., LEE S., *Nature*, 374 (1995), 792.
- [3] BRUCE D.W., *Accounts Chem. Res.*, 33 (2000), 831.
- [4] MOULTON B., LU J., HAJNDL R., HARIHARAN S., ZAWOROTKO M.J., *Angew. Chem. Int. Edit.*, 41 (2002) 2821.
- [5] CLEVERTY A.M., WARD M.D., *Accounts Chem. Res.*, 31 (1998), 842.
- [6] RASHIDI RANJBAR Z., MORSALI A., *J. Mol. Struct.*, 936 (2009) 206.
- [7] MORSALI A., TADJARODI R., MOHAMMADI R., MAHJOUB A.R., *Z. Krist.-New Cryst. St.*, 216 (2001) 379.
- [8] MAHJOUB A.R., MORSALI A., *J. Coord. Chem.*, 56 (2003), 779.
- [9] MORSALI A., PAYHEGHADER M., POORHERAVI M.R., JAMALI F.Z., *Z. Anorg. Allg. Chem.*, 629 (2003), 1627.
- [10] MORSALI A., MAHJOUB A. R., DARZI S. J., SOLTANIAN M. J., *Z. Anorg. Allg. Chem.*, 629 (2003), 2596.
- [11] MORSALI A., KEMPE R., *Helv. Chim. Acta*, 88 (2005), 2267.
- [12] XIAO H.P., MORSALI A., *Helv. Chim. Acta*, 88 (2005), 2543.
- [13] MORSALI A., MAHJOUB A.R., *Solid State Sci.*, 7 (2005), 1429.
- [14] MORSALI A., *Solid State Sci.*, 8 (2006), 82.
- [15] BECKMAN U., BROOKER S., *Coordin. Chem. Rev.*, 245 (2003), 17.
- [16] KLINGALE M.H., BROOKER S., *Coordin. Chem. Rev.*, 241 (2003) 119.
- [17] HAASNoot J.G., *Coordin. Chem. Rev.*, 200 (2000), 131.
- [18] WITHERSBY M.A. et al., *Inorg. Chem.*, 38 (1999), 2259.
- [19] BLAKE A.J., CHAMPNESS N.R., COOKE P.A., NICOLSON J.E.B., WILSON C., *J. Chem. Soc. Dalton*, (2000), 3811.
- [20] WITHERSBY M.A., BLAKE A.J., CHAMPNESS N.R., HUBBERSTEY P., LI W.S., SCHRODER M., *Angew. Chem. Int. Edit.*, 36 (1997), 2327.
- [21] NOTASH B., SAFARI N., KHAVASI H. R., AMANI V., ABEDI A., *J. Organomet. Chem.*, 693 (2008), 3553.
- [22] AKHBARI K., MORSALI A., *Coordin. Chem. Rev.*, 254 (2010), 1977.
- [23] SHELDRICK G. M. (2008), SADABS V2008/1, Bruker-AXS Inc, Madison, Wisconsin, USA.
- [24] SHELDRICK G. M., *Acta Crystallogr. A*, 64 (2008) 112.
- [25] Mercury 1.4.1, Copyright Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, 2001.
- [26] DEMKO Z.P., SHARPLESS K. B., *J. Org. Chem.*, 66 (2001), 7945.
- [27] HAZELL A., MCGINLEY J., TOFTLUND H., *Inorg. Chim. Acta.*, 323 (2001), 113.
- [28] YANG J., LIN C., WANG ZH., LIN J., *Inorg. Chem.*, 45 (2006), 8973.

Received 2013-09-25

Accepted 2013-12-02