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# A thallium(I) tetranuclear cubic cage unit in an interpenetrated supramolecular polymer: A new precursor for the preparation of $Tl_2O_3$ nanostructures

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### ABSTRACT

A new thallium(I) supramolecular polymer,  $[Tl_4(\mu_3-4-BN)_4]_n$  (1) [9-HBN = 4-hydroxy benzonitrile], with a disordered cubic cage structural unit has been synthesized and characterized. The single-crystal X-ray data of compound 1 shows one type of Tl<sup>1</sup> ion in the tetranuclear cubic cage structure with a coordination number of three. In addition to two intra cage thallophilic interactions in 1, each thallium(I) atom has a weak Tl···N secondary interaction with the nitrile group of the 4-BN<sup>-</sup> ligand. Finally the Tl-ions attain the  $O_3 Tl$ ···NTl<sub>2</sub> coordination sphere with a stereo-chemically 'active' electron lone pair on the metal. The self assembly between the benzonitrile groups of one cubic cage structure with an adjacent one with a Tl···N short contact, by  $\pi$ - $\pi$  stacking and weak hydrogen bonding interactions, results in the formation of a new interpenetrating thallium(I) supramolecular polymer. The thermal stability of 1 was studied by thermo gravimetric (TG) and differential thermal analyses (DTA). Nanostructures of thallium(II) oxide were prepared from a calcination process of compound 1 fine powder at 743 K. These nanostructures were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM).

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### 1. Introduction

During the last two decades supramolecular compounds and especially coordination polymers have received great attention and the number of their synthesized compounds is still growing, which is mainly due to their potential application in various fields such as microelectronics, non-linear optics, ion exchange, catalysis, gas storage, separation and luminescence [1-6]. In modern coordination chemistry the role of most metals as clustering centers for ligands appears to be predictable and the coordination number and the coordination geometry can be extrapolated for most of the common metal/ligand combinations with quite high certainty. Although this is generally true, the situation is surprisingly difficult for main group metals in their low oxidation states, in which they are assigned lone pairs of electrons [7–12]. Although such a pair of s electrons beyond a completed shell is always stereoactive in the thallium(I) complexes with a hemi-directed environment, lower coordination number (three to five) and an obvious gap in Tl<sup>I</sup> coordination sphere, this activity cannot be predicted in complexes with higher coordination number (6-12) and a holo-directed environment [13]. Formation of polymers with main group metal ions such as thallium(I) is disproportionately sparse when compared with those of other metals, but the chemistry and coordination behavior of thallium(I) ion is very unique and attractive [14], and the number of Tl<sup>1</sup> supramolecular compounds is very much lower than for other metal ions. Tl<sup>I</sup> favors the formation of neutral species with anionic ligands. One-dimensional polymers constitute a great portion of the thallium(I) supramolecular compounds, whilst twoand three-dimensional polymers are less common. This may be related to the existence of a vacant site on the thallium(I) environment and the hemi-directed coordination sphere of the Tl<sup>I</sup> ion due to the stereo-chemical activity of its lone pair, which was frequently observed, and effects related to the structure, size and rigidity of the ligands. In addition, thallium(I) usually favors the formation of Tl...Tl, Tl...C and Tl...H secondary interactions, especially on its vacant coordination sphere with the stereo-chemically active lone pair, which indicates that thallium(I) ions have the capacity to act as both a Lewis acid and a Lewis base [14]. Continuing our previous works on Tl<sup>I</sup> supramolecular compounds [15-22] and to extend the number of thallium(I) supramolecular compounds with other organic ligands, in this work we wish to report another supramolecular compound containing the Tl<sup>I</sup> ion, having a tetranuclear cubic cage unit, formed with the 4-hydroxy benzonitrile ligand (4-HBN). With phenolate derivative ligands, Tl<sup>1</sup> usually forms two structures: disordered cubic units, which are retained in the solution state with thallophilic interactions, and stair-like polymers. In this case we observed the tetranuclear cubic cage structure again. In addition to the synthesis and characterization of





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Scheme 1. The produced materials from the reaction of the 4-HBN<sup>-</sup> ligand with thallium(I) nitrate by two different methods and fabrication of thallium(III) oxide nanostructures from the resulting materials.

Table 1
Crystal data and structure refinement for compound $[Tl_4(\mu_3-4-BN)_4]$ (1)

Empirical formula	C <sub>7</sub> H <sub>4</sub> NOTI
Formula weight	322.48
T (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	tetragonal
Space group	I 4 <sub>1</sub> /a
Unit cell dimensions	
a (Å)	16.8343(18)
b (Å)	16.8343(18)
<i>c</i> (Å)	10.086(2)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å <sup>3</sup> )	2858.3(7)
Ζ	16
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	2.998
Absorption coefficient (mm <sup>-1</sup> )	22.522
F(000)	2272
Crystal size (mm <sup>3</sup> )	$0.13 \times 0.12 \times 0.11$
$\theta$ Range for data collection (°)	2.35-25.10
Index ranges	$-20 \leqslant h \leqslant 12$
-	$-18 \leqslant k \leqslant 20$
	$-12 \leq l \leq 11$
Reflections collected	1277
Independent reflections	$1032 [R_{int} = 0.2371]$
Absorption correction	semi-empirical from
	equivalents
Maximum and minimum transmission	0.1908 and 0.1578
Refinement method	full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	1277/1/92
Goodness-of-fit (GOF) on $F^2$	1.142
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0741$
	$wR_2 = 0.1958$
R indices (all data)	$R_1 = 0.0824$
· · ·	$wR_2 = 0.2001$
Largest difference in peak and hole ( $e Å^{-3}$ )	0.502 and -2.559
,	

this complex, a mixture of TlBr nanoballs and nanorods were prepared by water-in-oil microemulsion-based methodology [23]. A fine powder of compound **1** and TlBr nanostructures were used for the preparation of  $Tl_2O_3$  nanostructures.

### 2. Experimental

### 2.1. Materials and physical techniques

All reagents for the synthesis and analysis were commercially available and used as received. Microanalyses were carried out

Table 2	
Selected bond lengths (Å) and angles (°) for compound $[Tl_4(\mu_3-4-BN)_4]_n$ (1).	

Tl1-01	2.487(11)	01-Tl1-01 <sup>i</sup>	79.2(4)
Tl1-O1 <sup>i</sup>	2.674(12)	01-Tl1-01 <sup>ii</sup>	78.6(4)
Tl1-O1 <sup>ii</sup>	2.704(12)	01 <sup>i</sup> -Tl1-01 <sup>ii</sup>	65.1(4)

Symmetry transformations used to generate equivalent atoms; i: -y + 3/4, x + 1/4, z + 1/4; ii: -x + 1/2, -y, z + 1/2.

using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. The thermal behavior was measured with a PL-STA 1500 apparatus between 40 and 610 °C in a static atmosphere of nitrogen. Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. The intensity data were collected using graphite monochromated Mo K $\alpha$  radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$ . Structure solution and refinement was accomplished using the SHELXL-97 program packages [24]. The molecular structure plot and simulated XRD powder pattern based on single crystal data were prepared using Mercury software [25]. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromatized Cu Ka radiation. The samples were characterized with a scanning electron microscope with a gold coating.

### 2.2. Synthesis of $[Tl_4(\mu_3-4-HBN)_4](1)$ , preparation of its single crystals and $Tl_2O_3$ nanostructures

The 4-hydroxy benzonitrile ligand (2 mmol (0.238 g)) was dissolved in 20 ml methanol and this was mixed and stirred with a solution of 2 mmol (0.114 g) KOH in 3 ml H<sub>2</sub>O. A solution of 2 mmol (0.533 g) TlNO<sub>3</sub> in 5 ml H<sub>2</sub>O was then added to the mixture, and the resulting solution was refluxed for 4 h. After filtering, it was allowed to evaporate for several days, whereupon suitable yellow crystals were obtained. The crystals were washed with acetone and air dried, d.p. = 216 °C, yield: 0.373 g (58%). IR (selected bands; in cm<sup>-1</sup>): 421 m, 452 m, 544 m, 645 w, 703 s, 810 m, 836 s, 992 w, 1102 m, 1160 s, 1203 m, 1284 s, 1351 w, 1401 s, 1580 s, 2165 s. *Anal.* Calc. for C<sub>7</sub>H<sub>4</sub>NOTI: C, 26.05; H, 1.24; N, 4.34. Found: C, 25.82; H, 1.30; N, 4.27%. In order to obtain Tl<sub>2</sub>O<sub>3</sub> nanostructures, a fine powder of compound **1**, after well grinding single crystals of **1**, was calcinated at 743 K in a furnace and under a static atmosphere of air for 5 h.



Fig. 1. View of the TI environment; showing the disordered tetranuclear cubic cage secondary building unit in  $[Tl_4(\mu_3-4-BN)_4]_n$  (1).



**Scheme 2.** The coordination mode of the ligand 4-BN<sup>-</sup> in compound **1** (left) and the schematic representation of the tetranuclear cubic cage unit (right).

## 2.3. Preparation mixture of TlBr nanoballs and nanorods, by the microemulsion-based methodology with a cationic surfactant, and $Tl_2O_3$ nanostructures

Mixture of thallium(I) bromide nanoballs and nanorods were prepared by the microemulsion-based methodology with cetyltrimethylammonium bromide (CTAB) as a cationic surfactant [26]. In a typical procedure, two 10.70 ml microemulsion solutions were prepared by adding 1.54 ml 0.5 M TlNO<sub>3</sub> and 1.54 ml 0.5 M 4-HBNK aqueous solutions to a *n*-heptane/CTAB/*n*-propanol system  $(n-\text{propanol/CTAB} = 4.10 \text{ (molar ratio)}, H_2O/CTAB = 20 \text{ (molar ra$ tio), [CTAB] = 0.4 M), respectively, which were stirred for 30 min at 308 K. The 4-HBNK microemulsion became transparent, but the TlNO<sub>3</sub> microemulsion formed a white precipitate. After that, the two solutions were mixed slowly and stirred for another 60 min at 308 K. Two types of precipitates were distinguishable, a large amount of white solid, which was CTAB (confirmed by an IR spectrum comparison of CTAB and this white solid) and a small amount of a yellow-white crystalline solid which consisted of TlBr nanoballs and nanorods (confirmed by XRD pattern comparison of this compound with the standard patterns of thallium(I) bromide with a JCPDS card number of 08-0486). The 10.7 ml of this mixture was separated by centrifugation and the obtained product was redispersed in a mixture of ethanol and water. This isolation process was repeated five times to give purified TlBr nanostructures in a powdery form. In order to obtain Tl<sub>2</sub>O<sub>3</sub> nanostructures from this precursor, half of this precipitate was calcinated at 873 K in a furnace and under a static atmosphere of air for 5 h. The black fine powder obtained was identified as Tl<sub>2</sub>O<sub>3</sub> nanostructures, confirmed by an XRD pattern comparison of this compound with the standard patterns of thallium(III) oxide with a JCPDS card number of 30-1351. Another 10.7 ml of the mixture was transferred to a 30-ml Teflon-lined stainless-steel autoclave and kept at 373 K for 1 h. After being cooled to room temperature, nanostructures of thallium(I) bromide (yellow-white crystalline products) were separated by centrifugation, and washed with deionized water and absolute ethanol several times, and then dried at 353 K for 6 h.

### 3. Results and discussion

#### 3.1. Structure description

Scheme 1 shows the reaction between thallium(I) nitrate and 4-HBNK by two different methods.

The reaction between 4-hydroxy benzonitrile (4-HBN). KOH and subsequently Tl<sup>I</sup>(NO<sub>3</sub>) provided crystalline materials of the general formula  $[Tl_4(\mu_3-4-BN)_4]_n$  (1). Determination of the structure of this compound by X-ray crystallography (Tables 1 and 2) showed the compound to have a novel tetranuclear cubic cage unit (Fig. 1 and Scheme 2) containing four Tl<sup>+</sup>-ions with coordination numbers of three. The Tl atoms are coordinated by three phenolic oxygen atoms with Tl-O distances of ca. 2.48-2.70 Å. The phenolic oxygen atom of the '4-BN<sup>-</sup>' ligand acts as bridging group (totally with three bonding interactions, Fig. 1 and Scheme 2). There are interactions between Tl1 and the two other thallium atoms in the cage. The distances between them are 3.833 Å, smaller than the sum of van der Waals radii of two Tl<sup>1</sup> ions [27]. The distances between the other thallium atoms within the cage are 4.510 Å, longer than the sum of van der Waals radii of two Tl<sup>1</sup> [14]. Hence, two metallophilic Tl…Tl interactions for the Tl1 atoms in compound  $[Tl_4(\mu_3-4-BN)_4]_n$  may be considered. Each Tl<sup>4</sup> ion also has a short contact with the nitrogen atom of the 4-BN<sup>-</sup> ligand (3.166 Å). Thus, the Tl-ions in this compound have an  $O_3$ **Tl**···NTl<sub>2</sub> coordination sphere. In  $[Tl_4(\mu_3-4-BN)_4]_n$ , the lone pair of the Tl(I) atoms is 'active' in the solid state. Indeed, the arrangement of O atoms suggests a gap or hole in the coordination geometry around the Tl(I) center (Fig. 1), a gap possibly occupied by a 'stereoactive' electron lone pair. Hence, the geometry of the nearest coordination environment of every Tl(I) atom is likely to be caused by the geometrical constraints of coordinated O and Tl atoms and by the influence of a stereo-chemically 'active' electron lone pair on the metal. Four thallium atoms and four oxygen atoms of 4-BN<sup>-</sup> anions form an interesting cage with a distorted cubic geometry (Fig. 1 and Scheme 2). As can be observed in Figs. 2 and S1, a  $\pi$ - $\pi$  stacking interaction between the parallel aromatic rings of adjacent units



**Fig. 2.** A fragment of three dimensional supramolecular polymer in  $[Tl_4(\mu_3-4-BN)_4]_n$  (1), showing the  $Tl \dots N$  short contact with green dashed lines and  $\pi - \pi$  stacking interactions between the parallel aromatic rings of adjacent units (TI = purple, O = red, C = gray, N = blue and H = white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** A fragment of three dimensional supramolecular polymer in  $[Tl_4(\mu_3-4-BN)_4]_n$  (1), showing lozenge channals of  $1.4 \times 2.1$  nm along the *b* axis (Tl = purple, O = red, C = gray, N = blue and H = white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Thermal behavior of the compound  $[Tl_4(\mu_3-4-BN)_4]_n$  (1).

has a distance of 3.838 Å, which can be considered as a normal  $\pi$ – $\pi$ stacking interaction [28,29]. A weak C-H ·· N hydrogen bonding interaction with a bond length of 2.749 Å and a bond angle of 162.70° stabilizes this supramolecular structure (Fig. S2). Self assembly between the benzonitrile groups of one cubic cage structure with an adjacent one with a Tl···N short contact, by  $\pi - \pi$  stacking and weak hydrogen bonding interactions, results in the formation of a new thallium(I) supramolecular polymer (Fig. 3). As could be observed in Fig. 3,  $[Tl_4(\mu_3-4-BN)_4]_n$  forms a 3D supramolecular compound with  $1.4 \times 2.1$  nm lozenge vacant channals along the b axis. These lozenge guest free channals could be observed along the a axis too (Fig. S3). Initially, this may indicate that this compound is porous, but further structural considerations indicate that these pores are occupied by another interpenetrating network, resulting in a completely packed supramolecular polymer with no vacant sites. A search in the Cambridge Structural Database (CSD) shows that there are only seven Tl<sup>I</sup> compounds with this tetranuclear cubic cage unit; [TlOCH<sub>2</sub>CF<sub>3</sub>]<sub>4</sub> [30], [Tl(µ<sub>3</sub>-OSiPh<sub>3</sub>)]<sub>4</sub> [31], [Tl(p-OC<sub>6</sub>H<sub>4</sub>- $NO_2$ ]<sub>4</sub> [32], [Tl(OC<sub>6</sub>H<sub>3</sub>(3,5-CF<sub>3</sub>)<sub>2</sub>)]<sub>4</sub> [33], [Tl(OCH<sub>2</sub>-tBu)]<sub>4</sub> [34],  $[Tl(\mu_3-OC_6H_3(2,4-Cl_2))]_4$  [21] and  $[Tl_4\{\mu_6-OC_6H_4(SO_2)C_6H_4O\}_2]_n$ [35]. Another search in the Cambridge Structural Database (CSD) shows that 1434 compounds have this tetranuclear cubic cage unit, and this unit (Scheme 2) could be observed for various different metal ions such as; Li<sup>+</sup> [36], Na<sup>+</sup> [36], K<sup>+</sup> [37], Mg<sup>2+</sup> [38], Ba<sup>2+</sup> [39], Ti<sup>2+</sup> [40], Cr<sup>3+</sup> [41], Mn<sup>2+</sup> [42], Fe<sup>2+</sup> [42], Co<sup>2+</sup> [42], Ni<sup>2+</sup> [42], Cu<sup>2+</sup> [43], Zn<sup>2+</sup> [42], Re<sup>+</sup> [44], Ru<sup>2+</sup> [45], Cd<sup>2+</sup> [46], Ag<sup>+</sup> [47], Pb<sup>2+</sup> [48], Yb<sup>2+</sup> [49] and Gd<sup>3+</sup> [50].

Thermo gravimetric (TG) and differential thermal analyses (DTA) of compound 1 single crystals shows that this compound is stable up to 185 °C in a static atmosphere of nitrogen (Fig. 4), at which temperature pyrolysis of compound 1 starts, and this continues up to 470 °C. Thus removal of 4-HBN<sup>-</sup> occurs between 185 and 470 °C and this pyrolysis process is accompanied by two exothermic effects at 230 and 420 °C. Fig. 5a shows the simulated XRD pattern from the single crystal X-ray data of compound 1 and Fig. 5b shows the XRD pattern of  $[Tl_4(\mu_3-4-BN)_4]_n$  fine powder, prepared from well grinding compound 1 single crystals. Acceptable matches, with slight different in  $2\theta$ , were observed between the simulated from singlecrystal X-ray data pattern (Fig. 5a) and the experimental powder X-ray diffraction pattern for a fine powder of compound 1 prepared by a grinding process (Fig. 5b). The results of the XRD powder patterns indicate that no structural changes occurred during the grinding process. In order to prepare Tl<sub>2</sub>O<sub>3</sub> nanostructures from the compound 1 precursor, a fine powder of compound 1, obtained from grinding compound 1 single crystals, was calcinated at 470 °C. Fig. 5c shows the XRD pattern of the residue obtained from the calcination process. The obtained patterns match the standard patterns of cubic Tl<sub>2</sub>O<sub>3</sub> with the lattice parameters a = 10.546 Å and



**Fig. 5.** XRD patterns; (a) simulated pattern based on single crystal data of compound **1**, (b) fine powder of compound **1** after the well grinding process, (c) nanostructures of  $Tl_2O_3$  prepared by the calcination process of compound **1** fine powder at 743 K, (d) TIBr nanostructures prepared by the reverse micelles technique and (e) thallium(III) oxide prepared by thermal treatment of TIBr at 873 K.

*z* = 16, which are close to the reported values, (JCPDS card number 30-1351). SEM images (Fig. 6) of the residue obtained from calcination of compound **1** fine powder at 743 K show that thallium(III) oxide with a nanostructural surface was formed. Microemulsion-based methodology, which uses reverse micelles of cationic surfactants such as cetyltrimethylammonium halides [CTAX, X = B (bromide), C (chloride)], is frequently used for the preparation of nanometer-sized metal-organic-frameworks (NMOFs) [51] and nanometer-sized metal-organic-frameworks (NMOFs) [23]. We used this methodology for the preparation compound **1** nanostructures from the initial reagents by the reaction of the TI<sup>+</sup> ion and 4-HBN<sup>-</sup> ligand, but the XRD pattern of the residue (Fig. 5d) matches the standard patterns of thallium(I) bromide, with the lattice parameters *a* = 3.9850 Å and *z* = 1, which are close to the



Fig. 6. SEM image of  $Tl_2O_3$  nanostructures, prepared by the calcination process of compound 1 fine powder at 743 K.



**Fig. 7.** SEM image of TIBr nanostructures, prepared by the reverse micelles technique using a cationic CTAB surfactant.



Fig. 8. SEM images of the  $Tl_2O_3$  nanostructural surface, prepared by calcination of TlBr nanostructures at 873 K.

reported values, (JCPDS card number 08-0486). A SEM image of the resulting product shows the formation of a mixture of TlBr nanoballs and nanorods (Fig. 7). Heat treatment of these TlBr nanostructures in a teflon-lined stainless-steel autoclave at 373 K for 1 h shows that an agglomeration process occurred, and the morphology and size distribution of these nanostructures changed (Fig. S4). Thus, this technique was not successful for the preparation compound 1 nanostructures. Calcination of TlBr powder at 873 K, resulted in the formation of black residue, the XRD pattern of which (Fig. 5e), matches with the standard patterns of thallium(III) oxide, with the lattice parameters mentioned above. The morphology, structure and size of the sample which was prepared by the calcination process on the TIBr nanostructures were investigated by scanning electron microscopy (SEM). The SEM images show the formation of cubic Tl<sub>2</sub>O<sub>3</sub> structures with a nanostructural surface (Fig. 8).

### 4. Conclusions

Thallium(III) oxide nanostructures were prepared from a calcination process of  $[Tl_4(\mu_3-4-BN)_4]_n$  (1) at 743 K. The microemulsion-based methodology was not successful for the syntheses of compound 1 nano-structures, and TlBr nanostructures were formed. Thermal treatment of the TlBr nanostructures resulted in the formation cubic structures of  $Tl_2O_3$  with a nanostructural surface. The Tl-ions in this compound have a  $O_3 Tl \cdots NTl_2$  coordination sphere with a stereo-chemically 'active' electron lone pair on the metal. Four thallium atoms and four oxygen atoms of  $4-BN^-$  anions form an interesting cage with a distorted cubic geometry. Self assembly between the benzonitrile groups of one cubic cage structure with an adjacent one with a Tl $\cdots$ N short contact, by  $\pi-\pi$  stacking and weak hydrogen bonding interactions, results in the formation of a new interpenetrating thallium(1) supramolecular polymer.

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### Appendix A. Supplementary data

CCDC 639612 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2011.06.027.

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