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# Organomercury derivatives of the 2,4,6-trimercaptotriazine ($H_3$TMT). X-ray crystal structure of $(HgMe)_3$(TMT)

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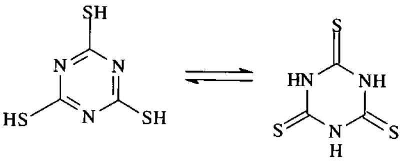
## Abstract

By reaction of RHgCl with $Na_3(C_3N_3S_3)·9H_2O$, organomercury derivatives of formulae $(HgR)_3(C_3N_3S_3)$ (R = Me, Et), have been synthesized and characterized. The methyl-derivative has been completely studied by X-ray diffraction analysis. The crystal and molecular structure consists of discrete $(HgMe)_3(C_3N_3S_3)$ units, where the triazine ligand is linked through the sulfur atoms to three HgMe moieties in a “manxane” arrangement. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* 2,4,6-Trimercaptotriazine; Methylmercury; X-ray structure.

## 1. Introduction

As remediation of heavy metal pollution is today becoming a worldwide necessity, many compounds are marketed to precipitate heavy metals from waste effluents and natural waters [1]. The trisodium salt nonahydrate of 2,4,6 trimercaptotriazine ($H_3$TMT) (already referred to as trithiocyanuric acid and existing in either thiol or thione forms (Scheme 1)) is quite a widespread reagent for precipitating divalent and univalent heavy metals from waters [2]. Only recently systematic investigations of the formation and stability of main group and transition metal TMT compounds have been undertaken [1,3]. However, apart from a few examples of complete X-ray characterizations, the chemical information is often limited due to the poor solubility of the products.



Scheme 1.

The TMT ligand, bearing three N,S donor sets, can display a great versatility of coordination. As a matter of fact it can use from one to all the six of its donor atoms, in mono- [4–8] and polynuclear complexes [7–13]. Its capability to act as a bridging ligand is also shown in polymeric compounds [13–15].

Additional interest about the TMT ligand stems from the fact that supramolecular organic systems with layered and channel structures can be obtained by the simple cocrystallization of the 2,4,6-trimercaptotriazine with different organic molecules suitable to form hydrogen bonding interactions [16].

Owing to our interest in the field of organomercury chemistry [17], we now report on the interaction of TMT with the exceedingly toxic organomercury derivatives RHgCl (R = $CH_3$, $C_2H_5$). Some organometallic Sn(IV) trimercaptotriazine derivatives have been recently reported [10].

## 2. Experimental

### 2.1. General materials

MeHgCl, EtHgCl from Strem Chemicals, and $Na_3(TMT)·9H_2O$ from Aldrich, were used as received. $H_3$TMT was prepared as previously reported [3].

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### 2.2. Syntheses

#### 2.2.1. Synthesis of $(HgMe)_3(TMT)$ (**1**)

To a solution of MeHgCl (1 mmol, 0.251 g) in MeOH (10 ml) was added dropwise, under continuous stirring, a solution of $Na_3(TMT)\cdot 9H_2O$ (0.33 mmol, 0.134 g) in the same solvent (20 ml). The colorless precipitate of prismatic crystals was filtered off, washed with water, then MeOH and dried in vacuo. The complex was recrystallized from DMF. Yield 0.240 g, 88%. Anal. Found: C, 8.78; H, 1.18; N, 5.12. Calc. for $C_6H_9Hg_3N_3S_3$: C, 8.78; H, 1.10; N, 5.12%. $^1$H-NMR (295 K, $d^5$-pyridine): $\delta$ 0.85 ppm (s, 9H, C$H_3$, $^2J_{HgH}=180$ Hz). $^{199}$Hg {$^1$H}-NMR (295 K, $d^5$-pyridine): $\delta$ 1735 ppm (s).

#### 2.2.2. Synthesis of $(HgEt)_3(TMT)$ (**2**)

The complex was analogously prepared. Colorless thin needles; yield 0.247 g, 86%. Anal. Found: C, 12.49; H, 1.87; N, 4.87. Calc. for $C_9H_{15}Hg_3N_3S_3$: C, 12.52; H, 1.75; N, 4.87%. $^1$H-NMR (295 K, $d^5$-pyridine): $\delta$ 1.69 ppm (q, 6H, C$H_2$CH$_3$, $^2J_{HgH}=185$ Hz); 1.35 ppm (t, 9H, CH$_2$C$H_3$, $^3J_{HgH}=252$ Hz). $^{199}$Hg {$^1$H} (295 K, $d^5$-pyridine): $\delta$ 1575 ppm (s).

#### 2.2.3. Reaction of $H_3TMT$ with MeHgCl–EtHgCl

Both complexes **1** and **2** can be alternatively prepared by reaction of RHgCl with $H_3TMT$ in pyridine, which acts as a base. Crystals are obtained by addition of *n*-butanol. Yields ca. 65–70%.

As an illustration of this method, we report in succession an attempt to prepare methyl–ethylmercury derivatives.

To a solution of MeHgCl (0.66 mmol, 0.165 g) and EtHgCl (0.33 mmol, 0.087 g) in Py (20 ml) was added dropwise, under continuous stirring, a solution of $H_3TMT$ (0.33 mmol, 0.058 g). Slow diffusion through the solution of *n*-butanol (30 ml) afforded the precipitation of colorless crystals (both prisms and needles). $^1$H and $^{199}$Hg {$^1$H}-NMR spectra (295 K, $d^5$-pyridine) of the mixture showed only the signals of **1** and **2** in the ca. 2:1 *ratio*, elementary analysis being consistent.

### 2.3. X-ray crystallography

Diffraction data of **1** were collected at room temperature on an Enraf Nonius CAD4 automatic diffractometer. Crystal data and data collection details are given in Table 1. After correction for background the intensities *I* were assigned standard deviations $\sigma(I)$ calculated using the value of 0.03 for the instability factor *k* [18]. The intensities were corrected for Lorentz and polarization effects and for absorption [19].

All the calculations were performed, using WINGX package [20] (SIR97 [21], SHELX97 [22], and ORTEP-III [23]). Atomic scattering factors were taken from Ref. [24] and an anomalous dispersion correction, real and imaginary part, was applied [25]. Direct methods and Fourier maps enabled the location of all the atoms. Full-matrix least-squares refinements on $F^2$ were carried out with anisotropic thermal parameters assigned to mercury and sulfur atoms. Hydrogen atoms were introduced in their calculated positions riding on their carbon atoms, with thermal parameters 20% larger than those of the respective carbon atoms. The function minimized during the refinement was $\Sigma w(F_o^2-F_c^2)$, with $w=1/[\sigma^2(F_o)^2+(0.0834P)^2]$, where $P=(\max(F_o^2,0)+2F_c^2)/3$.

Table 1
Crystal data and structure refinement for **1**

| | |
|---|---|
| Empirical formula | $C_6H_9Hg_3N_3S_3$ |
| Formula weight | 821.11 |
| Temperature (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Unit cell dimensions | |
| *a* (Å) | 8.497(6) |
| *b* (Å) | 9.747(7) |
| *c* (Å) | 9.804(7) |
| $\alpha$ (°) | 74.00(5) |
| $\beta$ (°) | 86.13(5) |
| $\gamma$ (°) | 67.47(5) |
| $V$ (Å$^3$) | 720.3(9) |
| $Z$ | 2 |
| $D_{calc}$ (Mg m$^{-3}$) | 3.786 |
| Absorption coefficient (mm$^{-1}$) | 32.301 |
| $F(000)$ | 708 |
| Crystal size (mm) | $0.25\times 0.20\times 0.10$ |
| Theta range for data collection (°) | 2.60–19.98 |
| Limiting indices | $-8\leq h<\leq 8$, $-8\leq k\leq 9$, $0\leq l\leq 9$ |
| Reflections collected/unique | 1335/1335 [$R_{int}=0.0000$] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 1335/0/100 |
| Goodness-of-fit on $F^2$ | 0.929 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1=0.0569$, $wR_2=0.1300$ |
| $R$ indices (all data) | $R_1=0.1056$, $wR_2=0.1402$ |

### 2.4. NMR measurements

$^1$H-NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer operating at 500.132 MHz. $^1$H chemical shifts are relative to external TMS. $^{199}$Hg {$^1$H}-NMR spectra were recorded on a Bruker AC-200 spectrometer, operating at 35.85 MHz. Chemical shifts are relative to external 0.1 mol dm$^{-3}$ $Hg(ClO_4)_2$ in 0.1 mol dm$^{-3}$ $HClO_4$. Downfield values of the chemical shifts are reported as positive.

## 3. Results and discussion

$Na_3(TMT)\cdot 9H_2O$ rapidly reacts with RHgCl (R = Me, Et) in water or methanol to afford a precipitate of $(RHg)_3(TMT)$:

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$Na_3(TMT)\cdot 9H_2O$ rapidly reacts with RHgCl (R = Me, Et) in water or methanol to afford a precipitate of $(RHg)_3(TMT)$:

$$Na_3(TMT)\cdot 9H_2O + 3RHgCl \xrightarrow{H_2O \text{ or } MeOH} (RHg)_3(TMT) + 3NaCl \qquad (I)$$

$$H_3TMT + 3RHgCl + 3Py \overset{Py}{\rightarrow} (RHg)_3(TMT) + 3(HPy)Cl \qquad (II)$$

Alternatively, the complexes can be prepared by reaction of $H_3TMT$ with RHgCl in pyridine, which acts as a base, and following addition of *n*-butanol as insolubilizing agent. In fact we have prepared the complexes in methanol, because the solubilities in water of MeHgCl and above all of EtHgCl are limited and the yield of the reactions in pyridine is smaller.

Apart from the molar ratio of the reagents, trisubstituted derivatives are always obtained. Very recently it has been pointed out that it is possible to control, through careful adjustment of the pH of reaction, the TMT/metal stoichiometries for divalent cobalt, copper and cadmium in aqueous solutions [7]. In the case of the organomercury derivatives, control of the pH seems to have no influence in determining the metal/TMT *ratio*, as the species $(RHg)_3(TMT)$ is always prevailing.

When we allowed $Na_3(TMT)$ to react with MeHgCl and EtHgCl together in molar *ratio* 1:2:1, a mixture of the $(MeHg)_3(TMT)$ and $(EtHg)_3(TMT)$ derivatives was formed.

Due to the water insolubility of **1**, $Na_3(TMT)$ appears to be very efficient to remove $MeHg^+$ ions from basic water solutions. In acidic solutions the addition of $Na_3(TMT)$ allows the precipitation of $H_3TMT$. Nevertheless, the high affinity of the mercapto group and the insolubility of $(MeHg)_3TMT$ favor the displacement of the equilibrium reaction (III) to the right, practically removing the most part of the methylmercury ions from the solution. As a matter of fact we have found that, upon addition of $Na_3(TMT)$ in saturated $D_2O$ solutions of MeHgCl at pH 1 (HCl) and stirring of the resultant mixture, after ca. 10 h only traces of $MeHg^+$ were detectable by $^1$H-NMR.

$$H_3TMT + 3MeHgCl \overset{H_2O}{\rightarrow} (MeHg)_3TMT + 3HCl \qquad (III)$$

The complexes are slightly soluble at room temperature in polar solvents, such as DMSO, DMF and pyridine. Recrystallizations of $(MeHg)_3(TMT)$ from DMSO, DMF or pyridine/butanol in excess afforded well-shaped crystals, which appeared generally twinned. Only after several attempts did we succeed in obtaining crystals suitable for an X-ray analysis from a pyridine/butanol recrystallization. No suitable crystals of the ethylmercury derivative have been obtained.

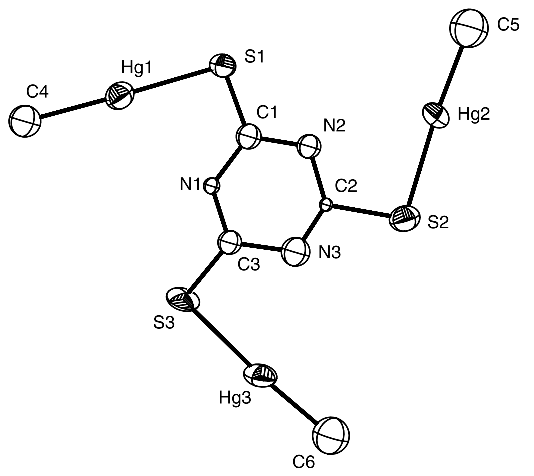

Fig. 1. Perspective view of the complex molecule $(HgMe)_3(TMT)$. ORTEP drawing with 30% probability ellipsoids.

Table 2
Selected bond lengths (Å) and angles (°) for **1**

| | |
|---|---|
| *Bond lengths* | |
| Hg(1)–C(4) | 2.13(4) |
| Hg(1)–S(1) | 2.37(1) |
| Hg(2)–C(5) | 2.06(4) |
| Hg(2)–S(2) | 2.39(1) |
| Hg(3)–C(6) | 2.09(5) |
| Hg(3)–S(3) | 2.38(1) |
| S(1)–C(1) | 1.67(4) |
| S(3)–C(3) | 1.65(3) |
| S(2)–C(2) | 1.74(3) |
| *Bond angles* | |
| C(4)–Hg(1)–S(1) | 178.2(12) |
| C(5)–Hg(2)–S(2) | 173.7(17) |
| C(6)–Hg(3)–S(3) | 174.8(15) |
| C(1)–S(1)–Hg(1) | 93.8(13) |
| C(3)–S(3)–Hg(3) | 95.8(14) |
| C(2)–S(2)–Hg(2) | 96.5(10) |

The molecular structure of **1** consists of discrete $(HgMe)_3(TMT)$ molecules where the TMT ligand is linked to three Hg–Me groups through the sulfur atoms. Fig. 1 shows a perspective view of the molecule and Table 2 reports selected bond distances and angles.

The molecule does not possess any crystallographic symmetry, however a pseudo $C_3$ symmetry can be envisaged for the $(NCSHgC)_3$ unit, which is practically planar in a “manxane” arrangement [26]. The S–Hg–C moieties are linear with angles ranging from 173.7(17) to 178.2(12)° and the mean values of the Hg–C (2.09(2) Å) and Hg–S (2.380(5) Å) bonds are fully comparable with those reported in the literature [27,28]. Moreover, the bending of the S–Hg bonds towards the ring nitrogen atoms, evidenced by the values of the Hg–S–C angles (93.8(13)–96.5(10)°), is indicative of an additional secondary interaction between the mercury and the nitrogen (Hg···N: 2.82(3)–2.87(3) Å). The mercury coordination can therefore be considered as T-shaped.

The title compound is fully isostructural with the already reported $(AuPPh_3)_3(TMT)$ [13] and $(SnR_3)_3$-(TMT) (R = Me, Ph) [10] complexes, however, while the Hg–S–C angles are only slightly smaller than the corresponding values in the tin derivatives (95.5(3)–99.3(1)°), they differ significantly from those in the gold complex (101.5(6)°). Here the presence of the more sterically demanding triphenylphosphine with respect to the methyl group may be considered responsible for the larger M–S–C angles.

The molecules $(HgMe)_3(TMT)$ are substantially discrete, even if intermolecular interactions of 3.5–3.7 Å between the mercury atoms and the sulfur of adjacent molecules are present (sum of the van der Waals radii of Hg and S is 3.30 Å) [29].

The NMR spectra are consistent with the coordination of $RHg^+$ by the sulfur atoms of TMT. The values of the $^2J_{HgH}$ coupling constants are considerably lower than those usually found for the mercapto-derivatives of $MeHg^+$ (130–160 Hz) [30]. This finding suggests a decreased strength of the Hg–S linkage in the present complexes in comparison with other alkylmercury mercaptides.

The different solubilities of mercury(II) and methylmercury(II) TMT-derivatives suggest a potential method to separate and analyze organometallic mercury. Investigations are in progress.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 166670. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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