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# Coordination network: synthesis, characterization, crystal structure and packing of thallium *m*-nitrobenzenesulfonate, Tl(*m*-$NO_2C_6H_4SO_3$)

Raj Pal Sharma[a,*], Ritu Bala[a], Rajni Sharma[a], Joanna Raczyńska[b], Urszula Rychlewska[b,**]

[a]*Chemistry Department, Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh 160014, India*
[b]*Faculty of Chemistry, Department of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań, Poland*

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## Abstract

Thallium(I) sulfate and sodium salt of *m*-nitrobenzenesulfonate when reacted in 1:2 molar ratio in water resulted in the formation of white crystalline solid Tl(*m*-$NO_2C_6H_4SO_3$). The solid-state structure for this product was established by single-crystal X-ray diffraction. Both Tl(I) cation and the sulfonate group display high co-ordinating ability: one thallium(I) cation is surrounded by nine oxygen atoms and one sulfonate anion is coordinated to six different thallium(I) cations. The crystal can be viewed as consisting of alternating double molecular organic and inorganic layers.

*Keywords:* Arylsulfonates; Coordination network; Layered materials; Thallium(I) complexes; X-ray structure; Spectroscopy

## 1. Introduction

Design and synthesis of new materials with specific applications is a major challenge to chemists. Though organophosphonates ($RPO_3^{2-}$) bear a strong structural analogy to the organosulfonates ($RSO_3^-$), these sulfonates drew less attention on the premise that they were weakly coordinating. However, organosulfonates have received a great attention in recent years because of their longstanding industrial applications as surfactants, dyes, fuel and lubricant detergents or antioxidants [1]. They have also been studied as potential liquid crystalline [2] and non-linear optical materials [3,4]. Major contributions in this area have been made by three groups: Squattrito [5], Shimizu [6] and Schreuer [7] with significant contribution by others [8]. While transition and non-transition metal sulfonates are widely investigated, thallium(I) sulfonates have received little attention probably because of their toxic effects.

Because of our interest in the Tl(I) chemistry [9], we report the synthesis, characterization, crystal structure determination and packing of thallium(I) *meta*-nitrobenzenesulfonate. Tl(I) chemistry is very interesting due to a variety of reasons: (i) thallium salt/complexes are often anhydrous, (ii) the lone pair present on thallium may or may not be stereochemically active [10], (iii) presence of high coordination number because of large size of thallium(I) ion, (iv) thallium(I) ethoxide used as strong base in preparative inorganic chemistry, (v) because of the ease with which Tl(I) can be monitored by spectroscopic, fluorescence, polarographic and especially nuclear magnetic resonance (NMR), (vi) in sharp contrast to alkali metals, this ion is well suited as best probe in biological systems [11].

Sulfonate anions are generally considered to be weakly interacting or non-interacting [12]. The nitro substituted arylsulfonate anion was chosen as a ligand because the extra nitro group provides additional ligating sites besides those of sulfonate oxygens. Judicious selection of *m*-nitrobenzenesulfonate as the counterion for the construction of a coordination network of Tl(I) ions is based on two specific aspects: (i) placing a nitro group and a sulfonate group at 120° apart provides required geometrical proximity for both these ligating/bridging moieties to interact simultaneously

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* Corresponding authors. Tel.: +91 172 2544433; fax: +91 172 2545074. ** Tel.: +48 61 8291268; fax: +48 61 8658008.
*E-mail addresses:* rpsharma@pu.ac.in (R.P. Sharma), urszular@amu.edu.pl (U. Rychlewska).

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with a given metal ion or to different metal ions to generate networks that mimic coordination polymers, (ii) the *ortho*- or *para*-nitro analogues become less rewarding as the nitro group can substantially reduce the negative charge distribution on the sulfonate group through resonance stabilization thereby weakening the metal–ligand ionic interactions. Besides this, their geometrical positioning may only be suitable for either exclusive intra (*ortho*-$NO_2$) or inter- (*para*-$NO_2$) molecular coordination with the metal ion. Thus, we hypothesized that Tl(*m*-nitrobenzenesulfonate) may provide a coordination network involving both nitro and sulfonate groups of the ligand.

## 2. Experimental

### 2.1. Material required

Analytical grade reagents were used without any further purification.

### 2.2. Instrumentation

C, H, N were estimated microanalytically by automatic Perkin Elmer 2400 CHN elemental analyser Infrared spectrum was recorded using Perkin Elmer spectrum RX FT-IR system by using Nujol mulls in NaCl plates.

### 2.3. Synthesis of $Tl(m\text{-}NO_2C_6H_4SO_3)$

One gram (0.0019 mole) of $Tl_2SO_4$ was dissolved in 25 ml water. In another beaker 0.8921 g (0.0038 mole) of sodium *m*-nitrobenzenesulfonate was dissolved in minimum amount of water. Both the solutions were mixed slowly. The white crystals appeared after 1 day, which were collected by drawing off the mother liquor and air-dried (quantitative yield). The newly synthesized complex salt is freely soluble in water and DMSO but insoluble in organic solvents like chloroform. The melting point of this novel salt is above 200 °C. Anal. Calcd for Tl(*m*-$NO_2C_6H_4SO_3$) Tl, 50.31%; C, 17.73%; H, 0.98%; N, 3.44%. Found: Tl, 50.03%; C, 18.02%; H, 1.06%; N, 3.23%.

### 2.4. X-ray measurements

Single crystals suitable for X-ray structure determination were colourless, shining needle shaped and stable in air. The data collection was performed at ambient temperature. KUMA Diffraction KM-4 diffractometer equipped with CCD detector was used for a small crystal of dimensions 0.15×0.15×0.03 mm. The distance between the crystal and CCD detector was 60 mm and the ω-scan was used (0.7° frame width). A hemisphere of data (836 frames) was collected. The transmission factors showed large variations for the crystal, between 1.00 and 0.40. The absorption correction was performed with the procedure contained within the CrysAlis software package [13]. The structure was solved by direct methods, in the SHELXS-97 program package [14] followed by full-matrix least-squares refinements on $F^2$. Non-hydrogen atoms were treated anisotropically. The hydrogen atoms were placed at calculated positions and refined in a so called 'riding model' with their $U_{iso}$ increased by a factor 1.2 compared to $U_{eq}$ of atoms to which they were bonded. The SHELXL-97 [15] system of programs was used throughout. Drawings were prepared using CCDC Mercury 1.2.1 [16]. Crystal and experimental details are listed in Table 1.

Table 1
Crystal data and structural refinement for Tl(*m*-$NO_2C_6H_4SO_3$)

| | |
|---|---|
| *Crystal data* | |
| Chemical formula | $C_6H_4NO_2SO_3Tl$ |
| Chemical formula weight | 406.53 |
| Cell setting | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ (Å) | 14.795(3) |
| $b$ (Å) | 8.241(2) |
| $c$ (Å) | 7.562(2) |
| $\beta$ (°) | 101.46(3) |
| $V$ (Å$^3$) | 903.6(4) |
| $Z$ | 4 |
| Density (g cm$^{-3}$) | 2.988 |
| Radiation type | Mo Kα |
| Wavelength (Å) | 0.71074 |
| No. of reflection for cell parameters | 4451 |
| $\mu$ (mm$^{-1}$) | 18.1 |
| Temperature (K) | 293 |
| Crystal form | Plate |
| Crystal size (mm) | 0.15×0.15×0.03 |
| Crystal colour | Colourless |
| *Data collection* | |
| Diffractometer | Oxford Diffraction KM4 CCD κ-geometry |
| Monochromator | Graphite |
| Data collection method | ω scans |
| No. of measured reflections | 7328 |
| No. of independent reflections | 1914 |
| No. of observed reflections | 1454 |
| Criterion for observed reflections | $I>2\sigma(I)$ |
| $R_{int}$ | 0.0391 |
| $\Theta_{max}$ (°) | 26.73 |
| Range of $h$, $k$, $l$ | $-18\rightarrow h\rightarrow 18$, $-10\rightarrow k\rightarrow 4$, $-9\rightarrow l\rightarrow 9$ |
| Absorption correction type | Empirical |
| $T_{min}$ | 0.395 |
| $T_{max}$ | 1.000 |
| *Refinement* | |
| Refinement on | $F^2$ |
| $R[F^2>2\sigma(F^2)]$ | 0.0290 |
| $wR(F^2)$ | 0.0435 |
| $S$ | 0.971 |
| No. of reflection used in refinement | 1454 |
| No. of parameters used | 127 |
| H-atom treatment | Riding model |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0.69 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | $-0.97$ |