The Crystal Structure of Thallium(I) Trithiocarbonate, Tl₂CS₃

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Dedicated to Professor Gerd Meyer on the Occasion of His 60th Birthday

Keywords: Thallium; Trithiocarbonate; Crystal structure; Powder diffraction; Raman spectroscopy; IR spectroscopy

Abstract. Thallium trithiocarbonate, Tl₂CS₃, was prepared by the reaction of Na₂CS₃ with TlNO₃ in aqueous solution. Tl₂CS₃ has a low solubility and is precipitated as an orange powder. DSC measurements show Tl₂CS₃ to be stable up to 155 °C. Above this temperature exothermic decomposition under evolution of CS₂ occurs. The crystal structure was determined based on powder diffraction data and Rietveld refinement (monoclinic, *C2/c*, *a* = 1143.33(1), *b* = 627.70(1), *c* = 916.03(1) pm, β = 118.77(1)°, *Z* = 4). The structure shows a close relationship and is isopointal to the structure.

ture of β -Na₂CS₃ (Henseler, Jansen 1992). Tl⁺ has an irregular nonacoordination. The overall arrangement of the ions can be described as being analog to the *anti*-CaF₂ structure type with Tl⁺ making up a strongly distorted primitive cubic array and CS₃²⁻ occupying one half of the cubical cavities. In the crystal, the D_{3h} symmetry of the CS₃²⁻ ions is lowered to the site symmetry C_2 and a slight angular deformation is observed. This loss of symmetry is also observed in the Raman and IR spectra by the splitting of degenerate modes.

Na₂CS₃ was prepared from sodium metal, ethanol, H₂S and CS₂

according to the procedure described by Yeoman [7]. Tl₂CS₃ was

prepared by precipitation from aqueous solutions of TlNO₃ and

Na₂CS₃ according to [7] and was obtained as an insoluble, orange

colored powder, which was filtered off, washed thoroughly with

Infrared spectra were recorded with a FT spectrometer Bruker IFS 113v and Raman spectra with a Bruker RFS 100 spectrometer. The

thermal analysis was performed between ambient temperature and

250 °C with a differential scanning calorimeter Netzsch DSC 204

F1 Phoenix. The sample was included in a closed aluminum cru-

Powder diffractograms were recorded with a Bruker D8 dif-

fractometer equipped with a positional sensitive detector and

Cu- $K_{\alpha 1}$ radiation in Debye–Scherrer geometry. Samples were filled

in thin-walled glass capillaries with a diameter of 0.2 mm and

11942 data points were recorded in the 2θ range up to 91.5°. In-

dexing of the diffractogram and determination of the lattice param-

eters was performed using the program WinXPow [8]. A structure

model was obtained by the program ENDEAVOUR [9]. A first

kind Chebyshev background function with 16 terms was applied as implemented in the GSAS program system [10]. Refinement of the lattice parameters, the atom positions, and the isotropic displacement parameters was performed with the program GSAS. A

Pseudovoigt function with 19 terms was used to fit the reflection

profiles for all 486 identified reflections. The observed and the

calculated powder diffractograms are shown in Figure 1. Crystallo-

graphic data are summarized in Table 1, the positional parameters

are included in Table 2, and important bond lengths and angles are

cible and heated with a temperature gradient of $10 \,^{\circ}\text{C} \cdot \text{min}^{-1}$.

Experimental Section

water and dried in vacuo.

Crystal Structure Analysis

Introduction

Trithiocarbonic acid, SC(SH)₂, forms a series of stable salts, of which the Na⁺, K⁺ [1], Ba²⁺, Cd²⁺, and the Tl⁺ salt are well known as the most stable [2]. The thermochemical properties of Tl₂CS₃ have been explored by its dissociation gas pressure resulting in the heat of formation of $-88 \text{ kJ} \cdot \text{mol}^{-1}$ [2]. Structural data on trithiocarbonates are rare. The structures of the hydrates K₂CS₃·H₂O [3] and Cs₂CS₃·H₂O [4] are known. Of the solvent free trithiocarbonates, only the structure of Na₂CS₃ has been determined on single crystals grown under solvothermal conditions from Na₂S and CS₂ in the presence of ethanol [5]. Na₂CS₃ has been shown to be a fairly good ion conductor at elevated temperatures.

In preceding vibrational spectroscopy studies on BaCS₃, PbCS₃, CdCS₃, and Tl₂CS₃ it was shown that the symmetry of the anion in the crystals must be lower than D_{3h} . Space groups with three fold rotation axes running through the anion should therefore not be taken into consideration [6]. The crystal structure of Tl₂CS₃ was so far not determined what may be caused by the low solubility. In the preparation process only fine, microcrystalline powders can be obtained. We succeeded now to ascertain the crystal structure based on powder diffraction data.

962

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Figure 1. Powder diffractogram of Tl_2CS_3 . Shown are the measured intensities, the calculated intensities, the background function, and the difference graph I_{obs} - I_{calcd} . The inset shows an enlargement of the high angle region of the diffractogram.

Table 1. Crystallographic data and details of structure determination for Tl_2CS_3 . Standard deviations are given in brackets and refer to the last significant digit.

Compound	Tl_2CS_3
Formula	CS ₃ Tl ₂
Formula weight $/g \cdot mol^{-1}$	516.93
Crystal system	monoclinic
Space group	C2/c
a /Å	1143.33(1)
b /Å	627.80(1)
c /Å	916.10(1)
βl°	118.77(1)
$V/Å^3$	576.40(2)
Number of formula units Z	4
Density (calcd.) $/g \cdot cm^{-3}$	5.96
μ / mm^{-1}	115.1
Diffractometer	Bruker D8
Radiation	Cu- K_{α} , $\lambda = 154.0598 \text{ pm}$
Temperature /K	293
Range of data collection /°	$4 < 2\Theta < 91.5$
Number of refined parameters	17
R _{wp}	0.0345
$R(F^2)$	0.0258
R(F) for all data	0.109
Largest difference peak and hole $/e \cdot A^{-3}$	+0.52 / -0.71

Table 2. Positional parameters and displacement parameters $U_{\rm iso}/10^6 \text{ pm}^3$ for the atoms in the structure of Tl₂CS₃. Standard deviations are given in brackets and refer to the last significant digit.

Atom	X	У	Ζ	$U_{\rm iso}$
С	0	0.0504(1)	0.25	0.022(5)
S(1)	0.3886(1)	0.4100(1)	0.0827(1)	0.0344(8)
S(2)	0	0.3205(1)	0.25	0.0256(8)
Tl	0.3398(1)	0.1775(1)	0.3696(1)	0.0409(2)

presented in Table 3. The graphical representations were made with the programs DIAMOND [11] and POV-RAY [12].



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T1-S(2)III	305.895(3)	$T1-S(1)^{II}$	408.372(3)
$Tl-S(1)^{IV}$	312.729(2)	$C - S(1)^{I}$	169.40(1)
$Tl-S(1)^{VI}$	326.489(3)	$C - S(1)^{VIII}$	169.40(1)
Tl-S(1)	328.056(2)	C - S(2)	169.58(1)
$Tl-S(1)^{I}$	330.585(2)		
$T1-S(2)^V$	339.281(2)	$S(1)^{I} - C - S(2)$	121.345(1)
T1-S(2)	360.564(3)	$S(2) - C - S(1)^{VIII}$	121.345(1)
$Tl-S(1)^{VII}$	372.426(4)	$S(1)^{I} - C - S(1)^{VIII}$	117.311(1)

Symmetry operations: I = 0.5 - x, -0.5 + y, 0.5 - z; II = x, -y, 0.5 + z; II = 0.5 - x, 0.5 - y, 1 - z; IV = x, 1 - y, 0.5 + z; V = 0.5 + x, -0.5 + y, z; VI = 1 - x, y, 0.5 - z; VII = 0.5 - x, 0.5 - y, -z; VIII = -0.5 + x, -0.5 + y, z.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (http://www.fiz-karlsruhe.de/ request_for_deposited_data.html) on quoting the CSD number 420223.

Results and Discussion

Crystal Structure of Tl₂CS₃

The crystal structure of Tl_2CS_3 is built of Tl^+ and CS_3^{2-} ions. The trithiocarbonate ions are located on twofold axes running through the atoms C and S(2). The ideal point symmetry D_{3h} of the ion is lowered to C_2 . The actual deviations are, however, small. The rotation axis causes the CS₃ group to be strictly planar. The two independent C-Sbonds differ by only 0.2 pm and the two independent S-C-S angles are 117.3° and $2 \times 121.3^{\circ}$. In the structure, all CS₃ groups are in a parallel arrangement with the Tl⁺ ions located between these planes (Figure 2). Taking into account the position of the carbon atoms, within a sphere of radius 470 pm the Tl⁺ ions are coordinated by four CS_3^{2-} ions. Expanding this sphere to a radius of 560 pm brings two additional anions into the coordination sphere. Three of the anions act as monodentate ligands with one coordinating sulfur atom and three as chelating ligands with two coordinating sulfur atoms giving the Tl⁺ ion the coordination number 9 forming a rather irregular polyhedron (Figure 3). The respective TI-S distances are in the range between 305.9 and 408.4 pm.

The crystal structure is closely related to the structure of β -Na₂CS₃ [5]. A significant difference is the lower coordination number of the Na⁺ ion in comparison to Tl⁺. Both structures can be derived from the *anti*-CaF₂ or Li₂O structure type. The Tl⁺ ions form a distorted primitive cubic array with every second cubical cavity filled by a CS₃²⁻ ion (Figure 4). The distortion from the cubic arrangement, however, is stronger in the case of Tl₂CS₃ than for β -Na₂CS₃. Since both structures share the same space group type and have comparable lattice constants and atom positions, the structure relation of Tl₂CS₃ and β -Na₂CS₃ is best characterized as isopointal [13].



Figure 2. The unit cell of Tl_2CS_3 . The atoms are represented by displacement spheres drawn with radii scaled to enclose a probability density of 50 %.



Figure 3. The coordination polyhedron around the Tl^+ ion in the structure of Tl_2CS_3 . For symmetry operations see legend of Table 3.

 Tl_2CS_3 does not show a structure relation to its oxygen containing congener thallium(I) carbonate. The structure of



Figure 4. Alternative view on the structure of Tl_2CS_3 to point out the relation to the CaF₂ structure type. The distorted cubical net made up by the Tl⁺ ions is shown, and the CS_3^{2-} ions occupying one half of the cubical-shaped interstices. Additionally, the crystal-lographic unit cell is shown with thick lines.

 Tl_2CO_3 is made up of layers -Tl-CO_3-Tl- \Box -Tl-CO₃- with a hexagonal closest packing of the Tl⁺ ions and CO₃²⁻ filling all octahedral holes in every second layer [14]. Tl₂CO₃ has a structural arrangement of the *anti*-CdI₂ or Ag₂F type. This shows the effect of the harder, less polarizable cabonate ion in comparison to the soft trithiocarbonate. The harder anion polarizes the Tl^I ion with the result of a pronounced lone pair effect and a van der Waals gap in the structure. In the structure of Tl₂CS₃ the Tl⁺ ion does not exhibit a distinct stereochemical effect of the lone electron pair.

Thermal Properties

The thermal properties of Tl_2CS_3 have been investigated by a DSC measurement, which showed thermal stability and no sign of phase transitions up to 150 °C. With an onset temperature of 155 °C an exothermic decomposition process over a broad temperature range of 50 °C accompanied by evolution of gas (CS₂) is detected. The thermal stability for Tl_2CS_3 is thus lower than for β -Na₂CS₃, which decomposes above 250 °C.



Vibrational Spectroscopy

The infrared spectra of trithiocarbonates including Tl₂CS₃ have already been recorded and a detailed analysis of the vibration modes was performed. The analysis showed that in the crystal the symmetry of the CS_3^{2-} ion is reduced from D_{3h} to $C_{2\nu}$ C₂, or C₈ [6]. The actual site symmetry C_2 for the CS₃ group confirms this prediction. In the infrared spectrum of β -Na₂CS₃ seven bands were found, which were attributed to four normal vibrations [5]. We performed additionally Raman spectra of Tl₂CS₃. Besides a poorly resolved broad lattice vibration band around 120 cm^{-1} , in the region between $300-1000 \text{ cm}^{-1}$, four sharp lines and one broader line were observed. Three of the four possible vibrations in the point group D_{3h} are Raman active. In the symmetry C_2 the degeneration of the asymmetrical valence vibration v_{asym} and the in-plane deformation mode is no longer valid. The out-of-plane deformation mode becomes Raman active and the symmetrical valence vibration becomes IR active. So one would expect six observable vibrations for the trithiocarbonate ion. The broad band in the Raman spectrum at 875 cm^{-1} can be attributed to two not resolved bands of the asymmetric valence vibration. The occurrence of an IR band at 884 cm⁻¹ can be explained by the factor group analysis. All internal vibrations of A and B character in point group C_2 are split in the factor group $C_{2h}(2/m)$ into two independent vibrations A_g and A_u and B_{g} and B_{u} , respectively, which are alternatively IR (u) or Raman (g) active. Thus, these two bands with a small but significant difference in energy may originate from the coupling of vibrations due to the presence of two independent CS_3^{2-} ions in the vibrational spectroscopic unit cell. In the IR spectrum an overlap of the out-of-plane deformation vibration and the symmetrical valence vibration at 494 cm^{-1} is present and the splitting of the in-plane deformation mode caused by the breakup of degeneracy cannot be resolved. Table 4 summarizes the observed bands in the vibration spectra and the respective attribution.

Conclusions

The crystal structure of thallium trithiocarbonate was determined by X-ray powder diffraction. The vibration spec-

Table 4. Raman and infrared frequencies of solid Tl₂CS₃ with attribution of molecular normal modes for the free CS₃²⁻ ion with point symmetry D_{3h} and for CS₃²⁻ in the crystal lattice with site symmetry C_2 .

Raman /cm ⁻¹	IR /cm ⁻¹	Attribution	D_{3h}	C_2
304	311	$\delta_{\rm in \ plane}$	E'	A + B
314	311	$\delta_{\rm in \ plane}$	E'	A+B
495	494	$\delta_{\text{out of plane}}$	A_2''	В
501	494	v _{sym}	A_1'	А
875	884	vasym	E'	A+B

tra are in line with the crystal structure and reveal the symmetry reduction of the CS_3^{2-} anion from D_{3h} to C_2 . A close structural relation is present to β -Na₂CS₃ but no relation to the structure of Tl₂CO₃ exists.

Acknowledgement

We are obliged to *D. Ernsthäuser* for the fruitful discussions on the interpretation of the vibrational spectra.

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Received: December 28, 2008 Published Online: April 9, 2009