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A Redetermination of the Trigonal Silver Fulminate Structure

BY DOYLE BRITTON

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA.

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Abstract. AgCNO, $M_r = 149.89$, trigonal, $R\bar{3}$, $a = 9.087$ (3) Å, $\alpha = 115.73$ (3)°, $V = 391$ (1) Å³, $Z = 6$, $D_x = 3.82$ (1) g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 73.5$ cm⁻¹, $F(000) = 408$, $T = 297$ (2) K, $R = 0.036$ for 665 unique reflections with $I > \sigma(I)$.

Experimental. The compound was prepared as described by Britton & Dunitz (1965) in the previous determination of this structure. A needle-shaped crystal $0.1 \times 0.1 \times 0.5$ mm was used for the data collection. Data were collected on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. 21 reflections with $11 < \theta < 22^\circ$ were used to determine the cell parameters. The previously reported space group, $R\bar{3}$, was assumed to be correct. Data were collected, using ω scans, in the range $0 < \theta < 26^\circ$ for one hemisphere and in the range $26 < \theta < 30^\circ$ for the entire sphere (ranges of h , k and l : -12 to 12). The intensities of 3108 different reflections were measured. Three check reflections measured every 5000 s of exposure time showed a linear decay of 19% over the entire data collection; this was corrected for. Absorption corrections were made based on ψ scans; maximum correction 5.3% in intensity. Equivalent reflections were combined to give 758 independent reflections ($R_{\text{int}} = 0.029$) of which 665 with $I > \sigma(I)$ were used in the calculations. The starting parameters were taken from the previous determination and were refined with full-matrix least squares on F values, using anisotropic thermal parameters for all atoms. Refinement converged with $R = 0.036$, $wR = 0.031$ and $S = 0.781$; $w = 1/\sigma^2(F)$ was calculated from $\sigma^2(I) = \sigma^2(I)_C + (0.02I)^2$, where $\sigma(I)_C$ is the standard deviation in I based only on counting statistics. In the final cycle of refinement $(\Delta/\sigma)_{\text{max}} = 0.01$, $(\Delta\rho)_{\text{max}} = 0.84$, and $(\Delta\rho)_{\text{min}} = -0.99$ e Å⁻³. Atomic scattering factors and anomalous-dispersion corrections for all atoms

Table 1. Atomic coordinates and equivalent isotropic thermal parameters

$$B_{\text{eq}} = \frac{1}{3}\pi^2 \sum_i U_i a_i^* a_i^* a_i^*$$

	x	y	z	B_{eq} (Å ²)
Ag	0.06334 (8)	0.15026 (8)	-0.20132 (8)	2.98 (2)
O	0.8771 (7)	0.7258 (7)	0.3849 (7)	3.0 (1)
N	0.6469 (8)	0.5150 (7)	0.2168 (7)	2.2 (1)
C	0.435 (1)	0.3221 (9)	0.061 (1)	2.3 (1)

Table 2. Interatomic distances (Å) and angles (°) for the orthorhombic and trigonal polymorphs of AgCNO

	Orthorhombic*	Trigonal†
Ag—C	2.183 (5)	2.151 (7)
		2.177 (7)
Ag—O	2.766 (2)	2.497 (4)
		2.731 (7)
		2.845 (8)
C—N	1.159 (8)	1.153 (7)
N—O	1.251 (6)	1.258 (7)
Ag—Ag	2.902 (1)	2.819 (1)
Ag—C—Ag	83.3 (2)	81.3 (3)
Ag—C—N	138.4 (1)	139.0 (4)
		139.4 (4)
C—N—O	180	179.2 (5)
C—Ag—C	180	166.0 (3)

* Barrick, Canfield & Giessen (1979).

† This work.

were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The computer programs used were from *TEXSAN* (Molecular Structure Corporation, 1985). The final positional parameters are given in Table 1.* Interatomic distances and angles are given in Table 2, where they are compared with

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54469 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

similar parameters from the orthorhombic polymorph (see below).

Related literature. The structures of the orthorhombic and trigonal polymorphs were originally determined by Britton & Dunitz (1965), who can be referred to for drawings of both polymorphs. The structure of the orthorhombic polymorph was redetermined by Barrick, Canfield & Giessen (1979). As shown in Table 2, the structural parameters for the fulminate ion are in complete agreement for the two polymorphs. The differences between the two

structures are confirmed; in particular the Ag—Ag distance in the cyclic hexamer of the trigonal form is significantly shorter than in the infinite polymer of the orthorhombic form and than in silver metal.

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Structure of a New Form of Triphenyltin(IV) Isothiocyanate

BY LIAN EE KHOO

School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia

AND XIAO-MING CHEN AND THOMAS C. W. MAK

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Abstract. Triphenyltin(IV) isothiocyanate, $(\text{C}_6\text{H}_5)_3\text{Sn.NCS}$, $M_r = 408.10$, orthorhombic, $Pna2_1$, $a = 8.966$ (2), $b = 14.552$ (5), $c = 13.085$ (4) Å, $V = 1707.4$ (7) Å³, $Z = 4$, $D_x = 1.587$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 16.6$ cm⁻¹, $F(000) = 808$, $T = 294$ K, $R_F = 0.042$ for 827 unique reflections. The complex features an infinite μ -1,3-thiocyanato-bridged zigzag chain running along the 2_1 axis with the Sn atom in a trigonal bipyramidal NC_3S -coordination environment. The bond angles at various junctions along the $[\text{Ph}_3\text{SnNCS}]_n$ polymeric chain in this orthorhombic form (I) are significantly different from those in the known form (II) belonging to space group $P2_1$, especially the Sn—N—C, C—S—Sn angles (by ca 10°); the bond lengths, the packing mode and the coordination geometry are all quite similar.

Experimental. To 4.1 g of crude triphenyltin isothiocyanate (m.p. 441–443 K) as prepared by Charland, Gabe, Khoo & Smith (1989) was added 1.1 g of sarcosine in 40 ml of ethanol (95%). The mixture was refluxed (20 min), cooled and kept in the freezer overnight. On filtration a solid (2.0 g, m.p. 465–467 K) was isolated. It was purified by repeated recrystallization (2 ×) in ethanol. Colorless needle-shaped crystals of triphenyltin isothiocyanate were obtained by slow evaporation of an ethanol solution.

A crystal of dimensions $0.16 \times 0.22 \times 0.24$ mm was mounted on a Nicolet $R3m/V$ diffractometer; data collected in the ω -scan mode ($3.0 \leq 2\theta \leq 50^\circ$) at room temperature (294 K); variable scan rate (1.51 – 9.01° min⁻¹); graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($10.3 \leq 2\theta \leq 16.6^\circ$); 1574 independent reflections measured ($0 \leq h \leq 9$, $0 \leq k \leq 17$, $0 \leq l \leq 15$), of which 827 reflections were considered observed [$|F_o| \geq 6\sigma(|F_o|)$]. Two standard reflections, 101 and 121, monitored after every 125 data measurements showed only random fluctuations within 1% of their mean values during data collection. Lorentz–polarization corrections and ψ -scan-based empirical absorption corrections (transmission factors 0.636–0.772) were applied. Structure solved by Patterson superposition and subsequent Fourier synthesis. The atoms of the tin and isothiocyanate group were refined anisotropically while the phenyl rings were handled as rigid groups. All H atoms were generated geometrically (C—H = 0.96 Å) and assigned the same isotropic temperature factor of $U = 0.10$ Å² in structure-factor calculations. The quantity minimized was $\sum w(F_o - F_c)^2$, where $w = [\sigma^2(F_o) + 0.0002|F_o|^2]^{-1}$. Final $R = 0.042$ and $wR = 0.043$ for 71 parameters and 827 observed reflections, $S = 1.318$, $(\Delta/\sigma)_{\text{max}} = 0.001$; largest peaks in the final difference map lie in the range 0.68 – -0.53 e Å⁻³.