



Synthesis and Crystal Structure of TeBr₂IBr

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The reaction of a mixture of Te, TeBr₄ and I₂ in molar ratios of 1:3:2 in a sealed evacuated ampoule at a temperature gradient range from 200°C to 180 °C yielded red crystals. The single crystal X-ray data for this compound showed that it had the TeBr₂IBr structure. In this compound, IBr is bonded to TeBr₂ and Br-I-Te has a nearly linear skeleton. The compound crystallizes in monoclinic system with a space group of P2₁/c and the lattice constants a = 16.234(2) Å, b = 11.082(4) Å, c = 15.147(3) Å, α = 90.03(1)°, β = 98.58(4)°, γ = 90.06(2)°.

Key Words: Adduct product, TeBr₂IBr, 3c-2e bond, Crystal structure.

INTRODUCTION

Chalcogens are the nearest elements to halogens with suitable reactivity. Although chalcogens are not metallic, but like transition metals they could form cluster compounds with chalcogen-chalcogen bonds. Compounds of Te₇²⁺, Te₄⁴⁺, Se₁₀²⁺ and Se₁₇²⁺, S₄²⁺ and S₈²⁺, have chalcogen-chalcogen bonds¹⁻⁶.

One of the routes to polychalcogen clusters makes use of a molten mixture of chalcogen and chalcogen tetrahalide in the presence of a suitable halide ion acceptor and eventually disproportionation reactions are carried out. A good example for this type is the reaction of a mixture of Se and SeCl₄ with ZrCl₄⁷ in a sealed tube at 130 °C that gives red crystals of Se₄(ZrCl₆) containing the polychalcogen cation Se₄²⁺. In this route, iodine is also used for disproportionation behaviour⁸ in the synthesis of Te₆I₂(WCl₆) from the reaction of Te with WCl₆ that containing the cation Te₆I₂²⁺.

We have found that the reaction of Te with TeBr₄ in the presence of I₂ in a sealed evacuated tube at 180 °C, resulted in the formation of TeBr₂IBr instead of polychalcogen cation.

EXPERIMENTAL

TeBr₄ was obtained from Te and Br₂⁹ and purified by sublimation. Tellurium was separated from oxidic impurities by melting and decanting. Iodine was mixed with P₄O₁₀ and then sublimed after 24 h.

Synthesis of TeBr₂IBr: Te (0.383 g, 3 mmol), TeBr₄ (4.025 g, 9 mmol) and I₂ (1.523 g, 6 mmol) were placed in a glass ampoule of 15 cm length and 2 cm diameter which is evacuated and sealed. The ampoule was placed in a horizontal tube furnace and heated for 5 h at 170 °C. Then it was placed

in temperature gradient from 200 °C to 180 °C within a week red, needle shaped crystals were transported to the colder part of the ampoule. The yield was nearly quantitative.

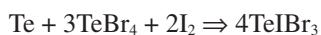
Crystal data and refinement details: [BrTeBr₂]. TeBr₃, M = 494.2, monoclinic, space group P2₁/c, a = 16.234(2) Å, b = 11.082(4) Å, c = 15.147(3) Å, α = 90.03(1)°, β = 98.58(4)°, γ = 90.06(2)°, V = 3053.6(5) Å³ and D_{calcd.} (Z = 4) of 2.184 Mg/m³, F(000) 484, μ (MoK_α) 11.706 mm⁻¹, crystal size: 0.35 mm × 0.20 mm × 0.25 mm, R = 0.0315, R_w = 0.0648.

Determination of the structure: Intensity data for the brown crystal with the approximate dimensions 0.35 mm × 0.20 mm × 0.25 mm were measured at 295 K on a Siemens R3m/V diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 12158 unique reflections were measured, 3848 of which with I > 2σ(I) were used in the refinement. The structure was determined using direct methods¹⁰ and subsequent difference Fourier maps and then refined on F² by a full-matrix least squares procedure using anisotropic displacement parameters for all atoms¹¹.

The final difference density map showed a maximum peak and hole of 2.215 and -2.534 e/Å³. Corrections for the Lorentz and polarization effects as well as the empirical correction for absorption using the SADABS programs were applied¹².

RESULTS AND DISCUSSION

The reaction of a mixture of Te, TeBr₄ and I₂ in molar ratios of 1:3:2 in a sealed evacuated ampoule at 180 °C yielded red crystals.



Application of single crystal X-ray diffraction on the brown crystals indicated the synthesis of a new compound with the molecular formula TeIBr₃. This compound crystallizes in monoclinic system with a space group of P2₁/c and the lattice constants $a = 16.234(2)$ Å, $b = 11.082(4)$ Å, $c = 15.147(3)$ Å, $\alpha = 90.03(1)^\circ$, $\beta = 98.58(4)^\circ$, $\gamma = 90.06(2)^\circ$.

X-Ray crystal and molecular structure of TeIBr₃: The crystallographic data for TeIBr₃ was tabulated in Table-1. The bond lengths and bond angles for TeIBr₃ were listed in Table-2.

TABLE-1 CRYSTAL DATA AND STRUCTURE REFINEMENT FOR TeBr ₂ I-Br	
Empirical formula	TeIBr ₃
Crystal colour	Red
Formula weight	494.2
Temperature (K)	295
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	
a (Å)	16.234(2)
b (Å)	11.082(4)
c (Å)	15.147(3)
α (°)	90.03(1)
β (°)	98.58(4)
γ (°)	90.06(2)
V (Å ³)	3053.6(5)
Z	4
D _{calc} (Mg/m ³)	2.184
Absorption coefficient (m m ⁻¹)	11.608
F(000)	484
Crystal size (mm)	0.35 × 0.20 × 0.25
Index ranges	-22 < h ≤ 22, -14 ≤ k ≤ 14, -16 < l ≤ 16
Number of reflections collected	12158
Independent reflections	4057 [R _{int} = 0.0483]
Max. and min. transmission	0.8943 and 0.3228
Refinement method	Full matrix least-squares on F ²
Goodness-of-fit on F ²	1.075
Final R indices [for 3789 reflections with I > 2σ(I)]	R ₁ = 0.0315, wR ₂ = 0.0648
R indices (all data)	R ₁ = 0.0357, wR ₂ = 0.0648
Largest difference peak and hole (e/Å ³)	2.215 and -2.534

TABLE-2 BOND LENGTHS (Å) AND BOND ANGLES (°) FOR TeBr ₂ I-Br			
Te-I	2.877(3)	Br(1)-Te-Br(2)	100.08(1)
I-Br(3)	2.681(4)	I-Te-Br(1)	95.43(5)
Te-Br(1)	2.432(2)	I-Te-Br(2)	97.28(5)
Te-Br(2)	2.441(2)	Te-I-Br(3)	177.54(1)

At first view, it could be gathered that TeIBr₃ was produced by the substitution of an I atom for one of the Br atoms in TeBr₄. However, the crystal structure of TeIBr₃ is quite different from that for other tellurium tetrahalides, TeX₄.

The molecular structure of TeIBr₃ is shown in Fig. 1. This compound has the abnormal molecular structure of TeBr₂I-Br, in which the I atom bonded to one of the Br atoms is also

bonded to Te, while in the hypothetical structure for TeIBr₃, the I and the three Br atoms should be bonded to the central Te atom. In TeBr₂I-Br, Te-I-Br with the bond angle of 177.54(1) has an approximately linear structure and TeBr₂I-Br has a trigonal pyramidal configuration geometry around Te atom with the bond angles Br(1)-Te-Br(2) 100.08(1), I-Te-Br(1) 95.43(5)° and I-Te-Br(2) 97.28(5)°. The bond angles for this compound are comparable to those in (CH₃)₂Se-I-I¹³, (CH₃)₂Se-I-Br, (C₆H₅)₂Se-I-Br¹⁴ and (C₆H₅)₂Se-I-I¹⁵; the bond angle for Te-I-Br has not been reported yet.

As seen in Fig. 1, from the three Br atoms present in the structure of TeBr₂I-Br, two are bonded directly to Te and the third one to the I atom. The Te-I bond length in this compound (2.877 Å) is close to that in Te₂I₂(WCl₆)₂, which is 2.76 Å¹⁶.

The I-Br bond length in this compound (2.681 Å) is greater than that in the non-coordinated IBr molecule (2.31 Å)¹⁷. The greater I-Br bond length in TeBr₂I-Br could be justified using the molecular orbital theory: transfer of electron density occurs from the non-bonding molecular orbital (HOMO) in TeBr₂ to the antibonding molecular orbital σ^* (LUMO) in IBr causes which bond length of I-Br would long. Therefore, TeBr₂I-Br could be regarded to be an adduct formed by the addition of the Lewis base TeBr₂ to the Lewis acid IBr.

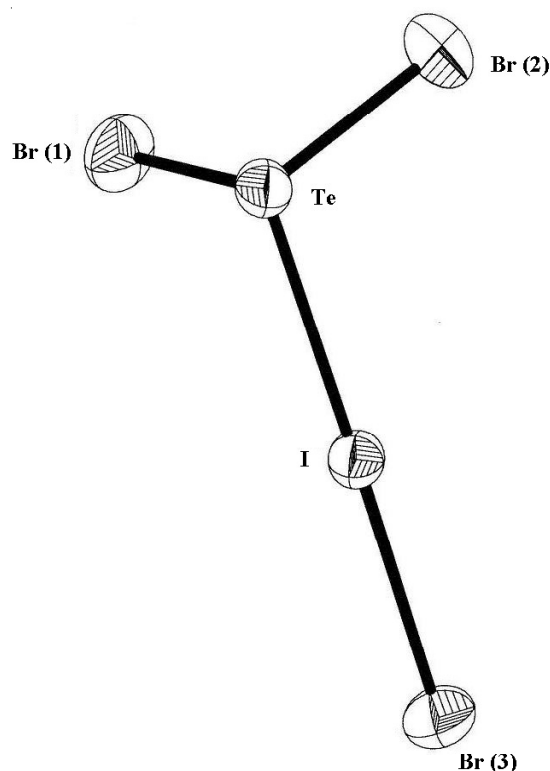


Fig. 1. Molecular structure of Br₂TeI-Br. The thermal ellipsoids are scaled to represent a probability density of 50 %

Conclusion

The reaction of a mixture of Te, TeBr₄ and I₂ in molar ratios of 1:3:2 in a sealed evacuated ampoule at 180 °C yielded red crystals of TeIBr₃. This compound has the abnormal molecular structure of TeBr₂I-Br, in which the I atom bonded to one of the Br atoms is also bonded to Te. In TeBr₂I-Br, Te-I-Br with the bond angle of 177.54(1) has an approximately

linear structure. According to molecular orbital theory transfer of electron density from the non-bonding molecular orbital (HOMO) in TeBr₂ to the antibonding molecular orbital σ^* (LUMO) in IBr causes which bond length of I-Br would long. TeBr₂IBr could be regarded to be an adduct formed by the addition of the Lewis base TeBr₂ to the Lewis acid IBr.

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