Synthesis and crystal structure determination of Br_2SeIBr polyhalogen–chalcogen

A A ALEMI* and E SOLAIMANI[†]

Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, Iran
[†]Department of Chemistry, Faculty of Science, University of Shahrood, Shahrood, Iran

Abstract. In this paper polyhalogen–chalcogen Br_2SeIBr was synthesized and the crystal structure was determined by single crystal X-ray diffraction method. This compound was prepared in the temperature range 150–50°C which was brownish-red in colour and crystallized in monoclinic crystal system and space group $P2_{1/c}$ with four molecules per unit cell. Lattice parameters were: $a = 6.3711(1)$, $b = 6.7522(2)$, $c = 16.8850(5)$ Å, $\alpha = \gamma = 90°$, $\beta = 95.96°$, $v = 722.45$ Å^3.

Keywords. Se; polyhalogen; chalcogen.

1. Introduction

For a long time, the multi-element compounds of main group elements were prepared and studied. The preparation of polyhalogen and polyhalogen–chalcogen compounds with different structural modifications which were the same as multi-element compounds of main group elements, were studied by most inorganic chemists. The preparation and study of $S_2I_4(MF_6)_2$, (M = As,Sb) (Murchie *et al* 1992), $Se_2I_4(AsF_6)_2 \cdot SO_2$ and the electronic structures of the eclipsed diselenium tetraiodide (2+) cation, containing two SeI_2^+ (Nandana *et al* 1982) and the study of $Te_6I_2^+$ cation in Te_6I_2 (WCl$_6$)$_2$ (Beck 1995), $[Se_6I]_n^+$ in $[Se_6I]_n \cdot n[MF_6]$ (M = As,Sb) (Nandana *et al* 1990) as polymeric cations of halogen–chalcogen and their crystallographic investigation prompted us to study the reaction of halogen and chalcogen group elements.

2. Experimental

2.1 *Preparation of SeBr$_4$*

Se powder and bromine were purchased from Merck company and $SeBr_4$ was prepared from the reaction of Se powder (0.1 g) with Br_2 (0.41 g) in a sealed ampoule glass of 20 cm length and 1.5 cm diameter in horizontal furnace at 80°C, after two days of heating the yellow crystals of $SeBr_4$ were found in the cold end of glass tube. All compounds were handled in argon filled glove box.

2.2 *Preparation of Br$_2$SeIBr*

Selenium (0.222 g), $SeBr_4$(1.12 g) and iodine (1.424 g) were filled in a glass ampoule of 25 cm length and 1.5 cm

diameter and heated in a horizontal tube furnace with a temperature gradient of 150–50°C after evacuation and sealing off the ampoule, for obtaining a good crystallization, at first the ampoule was heated for 5 h at 150°C, then we applied the temperature gradient as (0.04°C/min) to 100°C by heating for 48 h in such temperature, we also applied the other temperature gradient as (0.01°C/min) to 50°C. After 120 h heating in 50°C, we found brownish-red colour crystals of Br_2SeIBr in the cold end port of the ampoule.

2.3 *X-ray diffraction*

X-ray diffraction measurements were performed with Cu-Kα radiation on a Rigaku Multiflex diffractometer equipped with a curved graphite monochromator. Intensity data were collected by step scanning in the range of 2–90° at intervals of 0.02°.

3. Results and discussion

3.1 *Crystal structure determination*

Single crystal X-ray diffraction analysis of brownish-red crystal shows the crystallization in monoclinic system with space group $P2_{1/c}$ and cell constants are: $a = 6.3711(1)$, $b = 6.7522(1)$, $c = 16.8850(5)$ Å, $\alpha = \gamma = 90°$, $\beta = 95.96°$, $z = 4$, $v = 722.45$ Å^3 and $P_c = 4.047$ g/cm^3. Table 1 shows the crystal data and crystal refinement of Br_2SeIBr, table 2 shows the atomic coordinates and equivalent isotropic displacement parameters, table 3 shows bond lengths and bond angles of Br_2SeIBr and table 4 shows anisotropic displacement parameters.

The crystal structure of Br_2SeIBr molecule is illustrated in figure 1, as we can find from table 3 the Br(1)–

*Author for correspondence

Table 1. Crystal data and structure refinement for Br_2SeIBr.

Identification code	Br_2SeIBr
Empirical formula	Br_3ISe
Formula weight	445·59
Temperature	273(2) K
Wavelength	0·71073 Å
Crystal system, space group	Monoclinic, $P2_{1/c}$
Unit cell dimensions	$a = 6·3711(1)$ Å; $\alpha = 90°$
	$b = 6·7522(2)$ Å; $\beta = 95·96(2)°$
	$c = 16·8850(5)$ Å; $\gamma = 90°$
Volume	722·45(3) Å^3
Z, calculated density	4, 4·097 kg/m^3
Absorption coefficient	25·934 mm^{-1}
$F(000)$	768
Crystal size	$0·5 \times 0·45 \times 0·4$ mm
θ range for data collection	2·43–27·49°
Limiting indices	$-8 \leq h \leq 7, -8 \leq k \leq 8, -21 \leq l \leq 21$
Reflections collected/unique	13274/1653 [$R_{int} = 0·1623$]
Completeness to data	up to $\theta = 27·49°$ 99·9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1653/0/47
Goodness-of-fit on F^2	1·086
Final R indices [$1 > 2\sigma$ (1)]	$R1 = 0·0412, wR2 = 0·1088$
R indices (all data)	$R1 = 0·0466, wR2 = 0·1131$
Extinction coefficient	0·0122(8)
Largest diff. peak and hole	1·731 and $-1·687$ e Å^{-3}

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Br_2SeIBr.

	X	Y	Z	U(eq)
I	267(1)	1454(1)	3390(1)	34(1)
Se	$-3359(1)$	3502(1)	3699(1)	33(1)
Br(1)	3852(1)	$-413(1)$	3145(1)	41(1)
Br(2)	$-1642(1)$	6495(1)	3938(1)	49(1)
Br(3)	$-3547(1)$	3885(1)	4990(1)	46(1)

Table 3. Bond length [Å] and angles [°] for Br_2SeIBr.

I–Br(1)	2·6785(8)
I–Se	2·7879(8)
Se–Br(2)	2·3131(1)
Se–Br(3)	2·3223(1)
Br(1)–I–Se	177·35(3)
Br(2)–Se–Br(3)	100·91(4)
Br(2)–Se–I	94·59(3)
Br(3)–Se–I	98·00(3)

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for Br_2SeIBr. The anisotropic displacement factor exponent takes the form: $2\pi^2[h^2a^{*2}U11 + \ldots + 2\,hka\,{*}b^{*}\,U12]$.

	U11	U22	U33	U23	U13	U12
I	33(1)	33(1)	36(1)	1(1)	7(1)	0(1)
Se	29(1)	34(1)	38(1)	3(1)	7(1)	0(1)
Br(1)	36(1)	48(1)	39(1)	$-6(1)$	4(1)	8(1)
Br(2)	44(1)	38(1)	65(1)	$-6(1)$	14(1)	$-7(1)$
Br(3)	49(1)	54(1)	37(1)	6(1)	11(1)	$-4(1)$

of coordination with different distances (2·313 Å–4·172 Å) reveals that the Se atoms were surrounded by six halogen atoms (five bromine and one iodine atoms) as highly distorted octahedral. In between five bromine atoms (except number 3 with bond distance, 4·173 Å), all other atoms are in good agreement with Se and Br van der Waals radius (Huheey 1986).

3.2 *Molecular properties*

Table 2 indicates that in Br_2SeIBr molecule the I–Br bond length is 2·678 Å, but in a diatomic IBr molecule the bond is 2·485 Å (Macintyre 1994), so the existence of 0·193 Å difference can be dependent as the electron density distribution between IBr molecule and Br_2Se port of Br_2SeIBr molecule, it means that the electron density could be transferred from Se atom of Br_2Se part, into σ^{*} antibonding orbital of iodine atom of IBr, and the construction of Br_2SeIBr molecule will be the same as Lewis acid-base adducts, like Cl_2SeICl (Alemi and Solaimani 2000).

I–Se bond angle is 177·35° and the bond angles around Se atoms are: 100·91°, 94·59°, 98°, for Br(2)–Se–Br(3), I–Se–Br(2), I–Se–Br(3), respectively, so we can estimate that the Se atom surrounded by halogen atoms in pyramidal structure are in close conformity with Me_2SeIBr and Ph_2SeIBr (Godfrey *et al* 1997). Figure 2 shows the molecular structure of Br_2SeIBr and other bromine atoms from very closed molecules in unit cell. Study of the interactions between Se atoms and all bromine atoms in sphere

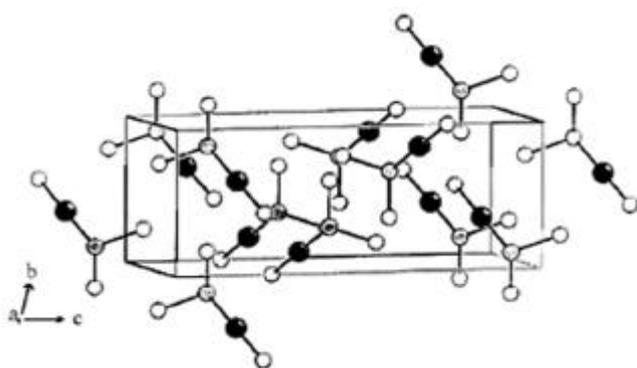**Figure 1.** A molecule of Br$_2$SeIBr including the coordination sphere of the selenium atom.

Figure 2. The unit cell of Br$_2$SeIBr.

Table 5. Bond lengths [Å] and angles [°] for some polyhalogens–chalcogens.

Formula	Se–I	I–Br	Se–Br
Br$_2$SeIBr	2·788	2·678	177
Me$_2$SeIBr	2·797	2·664	175·8
Ph$_2$SeIBr	2·809	2·640	177·29
C$_8$H$_7$NSSeIBr	2·814	2·633	177·9

Table 5 shows the bond lengths and bond angles of Br$_2$SeIBr and some other polyhalogen–chalcogen derivatives and in column one, we find the Se–I bond lengths increasing from top to bottom, but in column two the bond lengths decrease from top to bottom, although the Se–I–Br bond angles are approximately very close to 180°, but in Br$_2$SeIBr molecule the interaction between Br$_2$Se and IBr will be the same as lewis base and lewis acid adducts. The study of such kind of interaction in other polyhalogen–chalcogen shows the existence of a good relation between base strength of Br$_2$Se, Me$_2$S, Ph$_2$Se, C$_8$H$_7$NSSe for acid-base adducts in polyhalogen–chalcogen formation (Godfrey *et al* 1997). Investigation of Br$_2$SeIBr shows its close similarity to Cl$_2$SeICl (Alemi and Solaimani 2000) molecule that was recently prepared by our research group, and is also air sensitive and quickly change to opaque colour. Study of its colour change shows a complete deformation of its molecular structure, furthermore its solubility in organic solvents such as (CH$_2$Cl$_2$, CHCl$_3$, CCl$_4$) were examined, but in the presence of water it quickly dissociated to Br$^-$, SeO$_2$, I, etc.

3.3 *Elemental analysis*

Energy dispersion X-ray analysis of Br$_2$SeIBr molecule shows the bromine content as 18·2%, selenium as 24·14% and iodine as 54·53%.

4. Conclusions

It is concluded that the polyhalogen–chalcogen Br$_2$SeIBr with halogen character could be prepared at low temperature. Bond angle measurements show the Se–I–Br bond angle to be close to 180° and could estimate the presence of lewis base and lewis acid adducts in this compound.

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