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STRUCTURE OF RHODIUM SELENOBROMIDE $Rh_2Se_9Br_6$

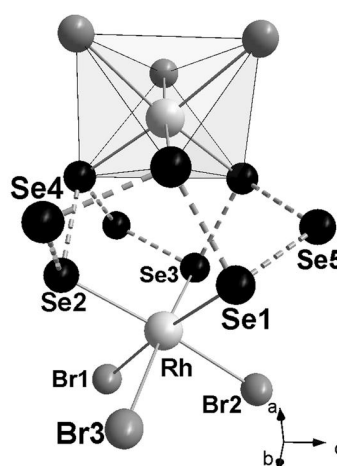
Reaction of interaction of crystalline hydrate of rhodium tribromide with excess of selenium monobromide present favourable conditions for the synthesis of dirhodium nonaselenium hexabromide $Rh_2Se_9Br_6$. The structure of the molecule was determined and were presented parameters of molecule. This compound has an allotropic form Se_9 , stabilized by two $RhBr_3$ molecules. $Rh_2Se_9Br_6$: tetragonal, $I4_1/a$ (no. 88), $a = 12.39996$ (12), $c = 24.8813$ (3) Å, $V = 3825.72$ (7) Å³, $Z = 8$, $R_I = 0.0181$, $R_F = 0.0184$, $R_p = 0.0354$, $R_{wp} = 0.0494$, $R_{exp} = 0.0235$, $\chi^2 = 4.43$, $T = 297$ K.

EXPERIMENTAL RESULTS AND DISCUSSION.

Dirhodium nonaselenium hexabromide $Rh_2Se_9Br_6$ was prepared from $RhBr_3 \cdot nH_2O$ (1 g) and Se_2Br_2 (10 ml). The synthesis was carried out in an L-shaped glass reactor. The lower part of the reactor, containing the reaction mixture, was subjected to heating whereas the upper part acted as a backflow condenser. The first stage of the synthesis was carried out at 80–90 °C for 120 h in the open reactor to remove the gaseous products H_2Se and HBr . At the second stage, the reactor was sealed and heating was continued at 100 °C for another 180 h. The solid product was separated from the liquid phase by transferring the mother liquor into the upper part of the reactor. Then the reactor was cooled down to 20 °C and opened. The solid phase was washed with CCl_4 and dried under vacuum.

For metastable solid-state allotropes of selenium only the cyclic Se_6 [1] and Se_8 [2–5] are observed and completely structurally characterized. But various "neutral" chalcogen ring-species can be stabilized in a solid matrix of metal halides, carbonyls, metal-organics, e.g. cyclic Te_6 in $Re_6Te_{16}Cl_6$ [6], Te_9 in $[Ru(Te_9)](InCl_4)_2$ [7], Se_7 in $[Re_2I_2(CO)_6(Se_7)]$ [8], Se_{12} in $[Ag_2Se_{12}][FAl(OC(C_5F_5))_3]_26C_6H_4F_2$ [9], etc. Recently, we reported on the first Se_9 cyclic cluster observed in solid state, which is stabilized by two $RhCl_3$ molecules in $Rh_2Se_9Cl_6$ [10]. Here we present another example of nonaselenium ring observed in isostructural compound $Rh_2Se_9Br_6$ (figure).

The selenium atoms are interconnected *via* covalent and near-covalent bonds ($\delta = 2.354$ – 2.457 Å) to form Se_9 rings in "crown" conformation. The longest bonds in the Se_9 -ring ($2 \cdot \delta(Se1-Se3) = 2.457$ Å



Structure of $Rh_2Se_9Br_6$ molecule.

Table 1
Data collection and hadling

Parameters	Hadling
Powder	Brownish black, size <0.04 mm
Wavelength	$CuK\alpha_1$ radiation (1.540598 Å)
μ	48.08 mm ⁻¹
Diffractometer	STOE STADI P (transmission mode)
$2\theta_{max}$, stepwidth	105.705°, 0.015°
$N(\text{points})_{measured}$	6848
$N(hkl)_{measured}$	1140
$N(\text{param})_{refined}$	87
Programs	STOE WinXPOW [11], N-TREOR09 [12], EXPO2009 [13], FullProf.2k [14], STRUCTURE TIDY [15], DIAMOND [16]

Table 2

Atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	<i>U</i> _{iso}
Rh(1)	16f	0.14074(20)	0.14243(19)	0.39158(7)	0.0163(15)
Se(1)	16f	0.0051(2)	0.3925(3)	0.32950(11)	0.018(2)
Se(2)	16f	0.0338(2)	0.1587(2)	0.47227(11)	0.026(3)
Se(3)	16f	0.3300(2)	0.1703(2)	0.12554(10)	0.018(3)
Se(4)	16f	0.3599(2)	0.0815(2)	0.04190(10)	0.023(2)
Se(5)	8e	0.0	0.25	0.26704(17)	0.021(3)
Br(1)	16f	0.0961(2)	0.0455(3)	0.20276(10)	0.036(3)
Br(2)	16f	0.1240(3)	0.0159(2)	0.06409(10)	0.023(2)
Br(3)	16f	0.3754(2)	0.5581(2)	0.09365(11)	0.028(2)

and $\delta(\text{Se2-Se2})=2.414 \text{ \AA}$) are between two $\mu\text{-Se}$ atoms, which belong to different $\text{Rh}[\text{Se}_3\text{Br}_3]$ distorted octahedra. These octahedra are formed by three Se atoms on one side and three Br atoms on the other side. Isolated "dimeric" molecular units $(\text{Br}_3\text{Rh})_2\text{Se}_9$ with local symmetry C_2 arrange so that 3D-packing with tetragonal symmetry appears. The Rh–Se bond distances of 2.389–2.417 Å are typical for rhodium μ -complexes with selenium, and the Rh–Br bond distances of 2.454, 2.483 and 2.522 Å agree well with mean Rh–Br[−] distance of 2.457 Å [17]. Data collection and handling, atomic coordinates and displacement parameters (in Å²) were presented in the tables 1, 2.

РЕЗЮМЕ. Реакция взаимодействия кристаллогидрата трибромида родия с избытком монобромида селена создает благоприятные условия для синтеза селенобромида родия $\text{Rh}_2\text{Se}_9\text{Br}_6$. Для данного соединения установлена структура и представлены параметры молекулы. Вещество содержит аллотропную форму Se_9 , стабилизированную двумя молекулами RhBr_3 . $\text{Rh}_2\text{Se}_9\text{Br}_6$ кристаллизуется в тетрагональной сингонии, $I4_1/a$ (no. 88), $a=12.39996(12) \text{ \AA}$, $c=24.8813(3) \text{ \AA}$, $V=3825.72(7) \text{ \AA}^3$, $Z=8$, $R_I=0.0181$, $R_F=0.0184$, $R_p=0.0354$, $R_{wp}=0.0494$, $R_{exp}=0.0235$, $\chi^2=4.43$, $T=297 \text{ K}$.

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РЕЗЮМЕ. Реакція взаємодії кристаллогідрату триброміду родію з надлишком моноброміду селену створює сприятливі умови для синтезу селеноброміду родію $\text{Rh}_2\text{Se}_9\text{Br}_6$. Для даної сполуки визначено структуру та представлено параметри молекули. Речовина містить алотропну форму Se_9 , стабілізовану двома молекулами RhBr_3 . $\text{Rh}_2\text{Se}_9\text{Br}_6$ кристалізується у тетрагональній сингонії, $I4_1/a$ (no. 88), $a=12.39996(12) \text{ \AA}$, $c=24.8813(3) \text{ \AA}$, $V=3825.72(7) \text{ \AA}^3$, $Z=8$, $R_I=0.0181$, $R_F=0.0184$, $R_p=0.0354$, $R_{wp}=0.0494$, $R_{exp}=0.0235$, $\chi^2=4.43$, $T=297 \text{ K}$.

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