

First coordination compounds of SeBr_2 with selenium-containing ligands: X-ray structural determination

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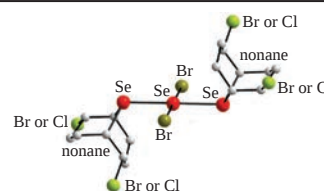
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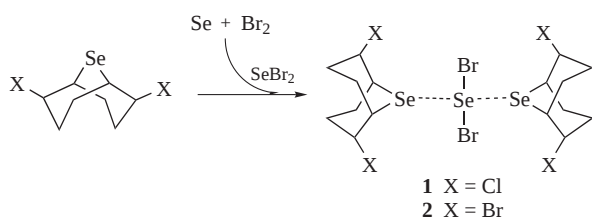
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The molecular structure of the coordination compounds of SeBr_2 with 2,6-dichloro- and 2,6-dibromo-9-selenabicyclo[3.3.1]nonane ligands was determined by X-ray powder diffraction analysis. The complexes have a less dense packing in comparison with that in an isostructural complex of SeCl_2 with 2,6-dichloro-9-selenabicyclo[3.3.1]nonane.



Selenium dichloride and selenium dibromide are used in the synthesis of organoselenium compounds including heterocycles.^{1–3} We carried out the transannular addition of selenium dichloride and selenium dibromide to *cis,cis*-1,5-cyclooctadiene furnishing 2,6-dihalo-9-selenabicyclo[3.3.1]nonanes as promising ligands for coordination chemistry.^{2,3} Diorganylselenide ligands form 2:1 complexes with transition metals.⁴ On the other hand, selenium dichloride and selenium dibromide form complexes as electron acceptor coordination centers.^{5–9} Complexes like $\text{SeX}_2 \cdot \text{L}_2$ or $\text{SeX}_2 \cdot (\text{L-L})$ were recently prepared by the reduction of selenium tetrahalides in the presence of sulfides [Me_2S , $\text{MeS}(\text{CH}_2)_2\text{SMe}$, $\text{MeS}(\text{CH}_2)_3\text{SMe}$ and *o*-(MeS) $_2\text{C}_6\text{H}_4$].⁵ Earlier, complexes of the former type ($\text{X} = \text{Cl}$, $\text{L} = \text{tetrahydrothiophene}$) were synthesized from SeCl_2 .⁶ A dimeric binuclear 1:1 complex of SeCl_2 with tetramethylthiourea was obtained using SeCl_2 or MeSeCl_3 (or SeCl_4).⁷ More numerous are divalent selenium complexes with strongly basic cationic iminium ligands coupled with different counterions⁸ or dications with the triflate counterion.⁹ The existence of the triselenium motif $\text{Se} \cdots \text{Se} \cdots \text{Se}$ and the formation of divalent or tetravalent selenium complexes with diorganyl selenides were an enigma to coordination chemists. An attempt to prepare such a complex by the reaction of selenium tetrahalides with dimethyl selenide led to the halogenation of the latter to Me_2SeX_2 and the reduction of SeX_4 to elemental selenium.⁵

Recently, we reported the synthesis and X-ray single crystal structural characterization of a novel complex of selenium dichloride with 2,6-dichloro-9-selenabicyclo[3.3.1]nonane, the first coordination compound of SeCl_2 with selenium ligands.³ Here,



Scheme 1

we present the structural characterization of selenium dibromide complexes with 2,6-dihalo-9-selenabicyclo[3.3.1]nonanes, the first coordination compounds of SeBr_2 with selenium ligands, using X-ray powder diffraction analysis.

Complexes **1** and **2** were synthesized in good yields by the reaction of *in situ* prepared SeBr_2 with 2 equiv. of 2,6-dihalo-9-selenabicyclo[3.3.1]nonane in CCl_4 or chloroform (Scheme 1).[†]

The molecular structures of complexes **1** and **2** are depicted in Figure 1.[‡] Both of the complexes belong to the C_i point group and have an inversion center of symmetry, which coincides with the central Se ion. Similarly to a related coordination compound of selenium dichloride with 2,6-dichloro-9-selenabicyclo[3.3.1]nonane (complex **3**), which was studied by single crystal X-ray diffraction analysis,³ complexes **1** and **2** crystallize in the same centrosymmetric space group and have the same chair–chair

[†] The melting points of complexes **1** and **2** were determined on a Boettius PHMK 05 apparatus. The IR spectra were taken on a Bruker Vertex 70 spectrometer in KBr.

Complex 1. A solution of bromine (0.16 g, 0.001 mol) in CCl_4 (4 ml) was added dropwise to a mixture of selenium (0.08 g, 0.001 mol) and CCl_4 (6 ml), and the mixture was stirred at room temperature until the disappearance of solid selenium. The resulting solution of SeBr_2 was added dropwise to a solution of 2,6-dichloro-9-selenabicyclo[3.3.1]nonane (0.52 g, 2 mmol) in CCl_4 (5 ml) for 20 min at 0 °C, and the mixture was allowed to warm to room temperature with stirring for 1 h. The formed precipitate was filtered, washed with chloroform and acetonitrile and dried to give complex **2**, yield 0.46 g (60%), mp 127–130 °C (decomp.). IR (ν/cm^{-1}): 2941, 2910, 1709, 1482, 1444, 1431, 1357, 1339, 1279, 1247, 1237, 1148, 1092, 1070, 945, 898, 877, 802, 773, 749, 736, 652, 603, 574, 453. Found (%): C, 25.90; H, 3.27; Se, 32.06; Br, 21.62; Cl, 19.03. Calc. for $\text{C}_{16}\text{H}_{24}\text{Br}_2\text{Cl}_4\text{Se}_3$ (%): C, 25.46; H, 3.20; Se, 31.38; Br, 21.17; Cl, 18.78.

Complex 2 was synthesized in a similar manner by the reaction of selenium dibromide with 2,6-dibromo-9-selenabicyclo[3.3.1]nonane in chloroform (93% yield), mp 140–143 °C (decomp.). IR (ν/cm^{-1}): 2943, 2905, 1631, 1480, 1442, 1428, 1355, 1335, 1278, 1252, 1237, 1141, 1089, 1060, 944, 895, 876, 789, 724, 698, 584, 549, 434. Found (%): C, 20.30; H, 2.69; Br, 51.25; Se, 25.27. Calc. for $\text{C}_{16}\text{H}_{24}\text{Br}_6\text{Se}_3$ (%): C, 20.60; H, 2.59; Br, 51.40; Se, 25.40.

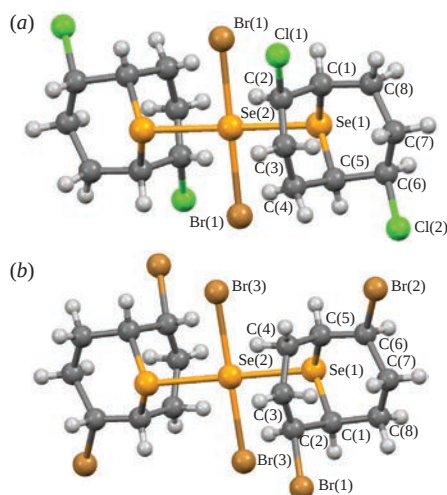


Figure 1 Molecular structure of complexes (a) **1** and (b) **2**. Selected bond lengths (Å) and angles (°): for **1**: Se(1)–Se(2) 2.656(3), Se(2)–Br(1) 2.565(2), Cl(1)–C(2) 1.82(1), Cl(2)–C(6) 1.81(1), Se(1)–C(1) 1.994(9), Se(1)–C(5) 1.954(8); C(1)–Se(1)–C(5) 91.0(2), Se(1)–Se(2)–Se(1) 180, Se(1)–Se(2)–Br(1) 90.37(8); for **2**: Se(1)–Se(2) 2.620(5), Se(2)–Br(3) 2.592(4), Br(1)–C(2) 1.88(2), Br(2)–C(6) 1.97(2), Se(1)–C(1) 2.09(2), Se(1)–C(5) 1.94(2), C(1)–Se(1)–C(5) 88.3(6), Se(1)–Se(2)–Se(1) 180, Se(1)–Se(2)–Br(3) 91.1(1).

conformation of the ligands with the equatorial halogen atoms. The central selenium atom in complexes **1** and **2** is characterized by a square planar configuration with the *trans* disposition of the selenium atoms of two selenobicyclo[3.3.1]nonane ligands.

The Se–C bond lengths in complexes **1** and **2** [1.954(7)–1.994(9) and 1.94(2)–2.09(2) Å, respectively] are close to those in related compound **3**. Like in complex **3**, the Se–Se bonds in complexes

† We failed to grow the crystals of complexes **1** and **2** suitable for single crystal X-ray structural analysis from chloroform or methylene chloride, in which they are slightly soluble. However, powder X-ray data (Bruker D2 Phaser ASX powder diffractometer) were sufficient for determining the structure of complexes **1** and **2**. The cell parameters and space group of complexes **1** and **2** were found by the TOPAS 4.2 program.¹⁰ The estimation of the number of non-hydrogen atoms from the cell volume led to 13–15 independent atoms in an asymmetric part of the unit cell. Therefore, it was concluded that the asymmetric part of the unit cell contained only one C₈H₁₂Br₂Se ion (C₈H₁₂Cl₂Se for complex **1**), one Se ion and one Br ion (Cl for complex **1**). The crystal structure was solved using a simulated annealing procedure applied to the randomized coordinate of Se/Br(Cl) ions and to the coordinates and orientation angles of C₈H₁₂Br₂Se (C₈H₁₂Cl₂Se) molecules. The final model of a crystal structure with the lowest *R*-factors was used for the Rietveld refinement in TOPAS 4.2.

Due to the low precision of powder diffraction data, we decided to refine a C₈H₁₂ molecule as a rigid body. The previously solved crystal structure of **3**³ was used to build a rigid molecule of C₈H₁₂. All Br, Cl and Se ions were refined without any restrictions, and their thermal parameters were refined isotropically. The thermal parameters of all C atoms have the same value of *B*_{iso}(C), which was refined, and the thermal parameters of hydrogen atoms have the values *B*_{iso}(H) = 1.5*B*_{iso}(C). After refinement, all thermal parameters had normal values. The refinement was stable and gave low uncertainty *R*-factors. The detailed powder XRD patterns for Rietveld structure analysis for each complex and the main processing parameters and refinement can be obtained from the authors.

For **1**: C₁₆H₂₄Br₂Cl₂Se₃, monoclinic, space group *P*2₁/*n*, *M*_r = 754.86, *a* = 7.5759(2), *b* = 11.2822(3) and *c* = 13.2457(4) Å, β = 90.303(2)°, *V* = 1132.14(6) Å³, *Z* = 2. 944 reflections collected and 22 refined parameters, final *R*-factors are *R*_{wp} = 5.41%, *R*_p = 2.77%, *R*_B = 1.90%, χ² = 1.95.

For **2**: C₁₆H₂₄Br₆Se₃, monoclinic, space group *P*2₁/*n*, *M*_r = 932.66, *a* = 7.6935(3), *b* = 11.3655(5) and *c* = 13.4757(5) Å, β = 91.550(2)°, *V* = 1177.88(8) Å³, *Z* = 2. 971 reflections collected and 22 refined parameters, final *R*-factors are *R*_{wp} = 5.95%, *R*_p = 2.57%, *R*_B = 1.47%, χ² = 2.32.

CCDC 1411937 and 1411944 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk>.

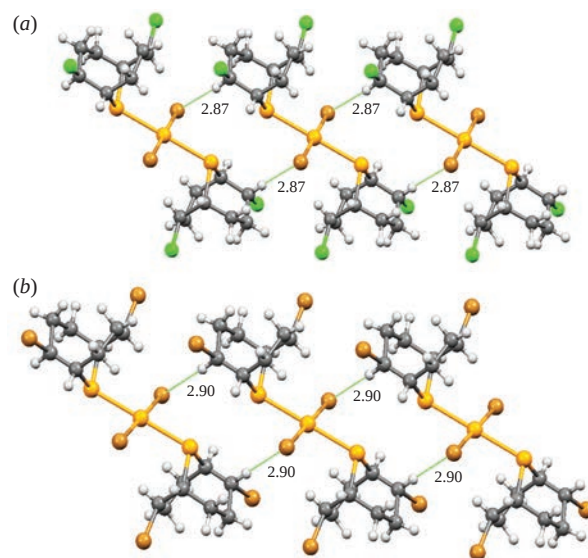


Figure 2 Short contacts in the crystal structures of complexes (a) **1** and (b) **2**.

1 and **2** amount to 2.620(5)–2.656(2) Å, which is 0.2 Å longer than that in the most of compounds containing a Se–Se bond.¹¹

The C–Se–C bond angles in compounds **1** and **2** are equal and very close to that in complex **3**.³ The Se–Se–Se fragment in all of these three complexes is linear. The Se–Se–Br bond angles in complexes **1** and **2** are almost right as the Se–Se–Cl bond angle in complex **3**³ or another similar complex of tetrahydrothiophene with SeCl₂.⁶

A comparison between the structures of complexes **1** and **2** reveals two differences. First, the Se–Se–Se bonds in complex **2** are 0.036 Å shorter than those in complex **1** suggesting stronger complexation in the former case. Second, the Se–Br bond in the central SeBr₂ moiety in complex **2** is 0.027 Å longer than that in complex **1**, also pointing to a stronger interaction of the central Se atom with the ligands in complex **2**.

In the crystal structure of complexes **1** and **2**, there are short contacts between the bromine and hydrogen atoms of the neighboring molecules (Figure 2). Note that the Br...H distances in complexes **1** (2.87 Å) and **2** (2.90 Å) are longer than the Cl...H contact in isostructural complex **3** (2.729 Å).³ Therefore, due to shorter intermolecular contacts, the latter complex has a more dense packing (*V* = 1084 Å³) in comparison with complexes **1** (*V* = 1132 Å³) and **2** (*V* = 1178 Å³).

Thus, the coordination compounds of SeBr₂ with selenium-containing ligands were prepared and their structure was characterized by X-ray powder diffraction analysis. We suggest that the formation of Se–Se–Se coordination bonds is important for the coordination chemistry and the design of novel selenium-containing supramolecular materials with probable conductivity.

The measurements were performed on the equipment of the Baikal Center for Collective Use of the Siberian Branch of the Russian Academy of Sciences.

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