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Expanded polycationic mercury–chalcogen networks in the layered compounds $\text{Hg}_3\text{E}_2[\text{MX}_6]$ ($E = \text{S, Se}$; $M = \text{Zr, Hf}$; $X = \text{Cl, Br}$)

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Abstract

The reactions of HgE ($E = \text{S, Se}$) with HgX_2 and MX_4 ($M = \text{Zr, Hf}$; $X = \text{Cl, Br}$) in evacuated glass ampoules lead to a series of isotopic compounds of the general formula $\text{Hg}_3\text{E}_2[\text{MX}_6]$ in the form of colorless ($X = \text{Cl}$) and light-yellow ($X = \text{Br}$) air-sensitive crystals. The crystal structures of $\text{Hg}_3\text{S}_2[\text{ZrCl}_6]$ (I), $\text{Hg}_3\text{S}_2[\text{HfCl}_6]$ (II), $\text{Hg}_3\text{Se}_2[\text{ZrCl}_6]$ (III), $\text{Hg}_3\text{Se}_2[\text{HfCl}_6]$ (IV), $\text{Hg}_3\text{S}_2[\text{ZrBr}_6]$ (V), and $\text{Hg}_3\text{Se}_2[\text{ZrBr}_6]$ (VI) were refined based on single-crystal data. All compounds crystallize in the monoclinic space group $P2_1/a$ with the lattice parameters $a = 662.18(2)$ pm, $b = 734.97(3)$ pm, $c = 1290.83(5)$ pm, $\beta = 91.755(2)^\circ$ for (I) and $a = 701.97(3)$ pm, $b = 756.79(3)$ pm, $c = 1350.99(6)$ pm, $\beta = 92.164(3)^\circ$ for (VI). The structures are built of $(\text{Hg}_3\text{E}_2)^{2+}$ layers stacked perpendicular to the c -axis. The polycationic layers consist of two-dimensionally linked 12-membered Hg_6E_6 rings in the chair conformation with linear coordinated Hg and trigonal pyramidal coordinated chalcogen atoms. Almost regular octahedral $[\text{MX}_6]^{2-}$ ions are embedded between the layers. This arrangement is closely related to the structure of $\text{Hg}_3\text{S}_2[\text{SiF}_6]$, which represents a higher symmetric congener. The structure relation is discussed using the supergroup–subgroup relation between space groups.

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Keywords: Mercury chalcogenide halides; Layered structure; Two-dimensional polycationic layer; Hexahalo metalate ions; Zirconium halides; Hafnium halides; Crystal structure

1. Introduction

Among the mercury chalcogenide halides, the ternary compounds $\text{Hg}_3\text{E}_2\text{X}_2$ are the most prominent and known for $E = \text{S, Se, Te}$ and $X = \text{Cl, Br, I}$. The crystal structures have been determined for the majority of the known compounds of this composition [1]. The predominant structural unit in these compounds is the trigonal EHg_3 pyramid, which forms a broad variety of polycationic structural units ranging from discrete cube-shaped Hg_{12}E_8 clusters to one-dimensional band-shaped, two-dimensional layered and three-dimensional network arrangements.

Despite the structures of the compounds of the $\text{Hg}_3\text{E}_2\text{X}_2$ family are separated in a polycationic Hg–chalcogen part and discrete halide ions, compounds with polycationic $[\text{Hg}_3\text{E}_2]^{2+}$ units and complex anions are rarely known. In the literature only the compounds $\text{Hg}_3\text{E}_2[\text{SO}_4]$ ($E = \text{S, Se}$) [2], $\text{Hg}_3\text{S}_2[\text{ClO}_4]_2$ [2],

$\text{Hg}_3\text{S}_2[\text{NO}_3]_2$ [3], $\text{Hg}_3\text{E}_2[\text{SiF}_6]$ ($E = \text{S, Se, Te}$) [4], and $\text{Hg}_3\text{S}_2[\text{CrO}_4]$ [5] are described.

The crystal structures of most of them are unknown. For $\text{Hg}_3\text{S}_2[\text{SO}_4]$ and $\text{Hg}_3\text{S}_2[\text{ClO}_4]_2$, the hexagonal crystal system and lattice parameters are mentioned, but space groups and further structural parameters were not determined. $\text{Hg}_3\text{S}_2[\text{SiF}_6]$, for which the crystal structure was solved by Puff and coworkers [4], crystallizes in the trigonal space group $P\bar{3}m$ with the lattice constants $a = 695$ pm and $c = 468$ pm. The structure is built of the typical Hg_3S pyramids which are connected to form layers in the a – b plane. Between the stacked layers, discrete octahedral ions $[\text{SiF}_6]^{2-}$ are located. $\text{Hg}_3\text{S}_2[\text{CrO}_4]$ was recently found as the mineral edoylerit in a Californian mercury mine [5]. The structure contains a three-dimensional $(\text{Hg}_3\text{S}_2)^{2+}$ network built from connected SHg_4 tetrahedra which hosts discrete $[\text{CrO}_4]^{2-}$ ions.

We attempted to synthesize further compounds with polycationic $[\text{Hg}_3\text{E}_2]^{2+}$ units and complex anions, and found that group 4 tetrahalides ZrX_4 and HfX_4 ($X = \text{Cl, Br}$) are suitable Lewis acceptors for halide ions in reactions with $\text{Hg}_3\text{E}_2\text{X}_2$. Here, we report on a complete series of isotopic compounds $\text{Hg}_3\text{E}_2[\text{MX}_6]$ with a layered

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structure closely related to that of the hexafluoro silicate $\text{Hg}_3\text{S}_2[\text{SiF}_6]$.

2. Experimental

2.1. Syntheses

Black mercury sulfide was prepared from mercury(II)chloride and H_2S [6]. HgSe was obtained from yellow mercury(II)oxide and elemental selenium [6]. The tetrahalides of zirconium and hafnium were prepared from the elements and freshly sublimated in vacuo before use [6]. All manipulations were performed in an argon-filled glove box. Glass ampoules were heated to 300°C in vacuo before charging. Mixtures of mercury(II)chalcogenide, mercury(II)halide and the tetrahalide of zirconium and hafnium, respectively, in molar ratio 2:1:1 were used as starting materials.

In a typical experiment, an ampoule of 16 cm length and 1.5 cm diameter was filled with 0.302 g (1.3 mmol) HgS , 0.176 g (0.65 mmol) HgCl_2 , and 0.151 g (0.65 mmol) ZrCl_4 . The ampoule was evacuated, sealed, and placed in a horizontal tube furnace of 60 cm length. With a rate of $40^\circ\text{C}/\text{h}$, a temperature of 360°C was reached and kept for 5 days. During this time, a temperature gradient of about 20°C along the ampoule was achieved by an asymmetric position of the ampoule in the oven with the starting materials in the warmer part at the oven center. After 5 days, the ampoule was taken out of the furnace and air-quenched.

The reaction temperatures were optimized for the different compositions and found as 360°C for $E=\text{S}$,

$X=\text{Cl}$, 475°C for $E=\text{Se}$, $X=\text{Cl}$, and 400°C for $X=\text{Br}$. The products crystallized in colorless ($X=\text{Cl}$) or light-yellow ($X=\text{Br}$) hexagonal or trapezium-shaped crystals in yields of 20–40% in the colder part of the ampoules. The major part of the deposited material consisted of zirconium and hafnium tetrahalides. Higher conversion rates could not be obtained in our experimental studies. Crystals of $\text{Hg}_3\text{E}_2[\text{MX}_6]$ are air and moisture sensitive and become yellow and opaque on exposure to air.

2.2. Structure determinations

Suitable single crystals were selected from the heterogeneous reaction product under dry atmosphere, filled in glass capillaries (diameter 0.3 mm) and mounted on a Nonius κ -CCD diffraction system using monochromated $\text{MoK}\alpha$ radiation ($\lambda = 71.073$ pm). The crystal dimensions, crystallographic data and details of the data collection are given in Table 1. All measured intensities were corrected for Lorentz and polarization effects. The space group $P2_1/a$ (no. 14) was determined from the symmetry of the diffraction lattice and the systematic absences with the aid of the program PLATON [7]. The non-conventional setting of the monoclinic cell was chosen for the possibility of a straightforward comparison with the higher symmetric hexafluoro silicate. The crystal structures were solved by direct methods (SHELXS-97, [8]), which revealed the positions of the heavier atoms Hg and Zr/Hf. The positions of the chalcogen and halide atoms were obtained from difference Fourier maps. The structures were refined by the full-matrix least-squares method (SHELXL-97, [9]) based on F^2 with anisotropic displacement

Table 1
Crystallographic data and refinement parameters for $\text{Hg}_3\text{S}_2[\text{ZrCl}_6]$ (I), $\text{Hg}_3\text{Se}_2[\text{ZrCl}_6]$ (III), $\text{Hg}_3\text{Se}_2[\text{HfCl}_6]$ (IV) and $\text{Hg}_3\text{Se}_2[\text{ZrBr}_6]$ (VI)

	$\text{Cl}_6\text{Hg}_3\text{S}_2\text{Zr}$ (I)	$\text{Cl}_6\text{Hg}_3\text{Se}_2\text{Zr}$ (III)	$\text{Cl}_6\text{HfHg}_3\text{Se}_2$ (IV)	$\text{Br}_6\text{Hg}_3\text{Se}_2\text{Zr}$ (VI)
Lattice constants (pm)	$a = 1290.83(5)$ $b = 734.97(3)$ $c = 662.18(2)$ $\beta = 91.755(2)^\circ$	$a = 1311.33(2)$ $b = 749.75(1)$ $c = 663.35(1)$ $\beta = 91.207(3)^\circ$	$a = 1309.50(6)$ $b = 749.90(4)$ $c = 662.72(3)$ $\beta = 91.992(3)^\circ$	$a = 1350.99(6)$ $b = 756.79(3)$ $c = 701.97(3)$ $\beta = 92.164(3)^\circ$
Volume (10^6 pm ³)	627.93(4)	652.01(1)	650.42(1)	717.19(5)
Z			4	
Calculated density (g/cm ³)	$\rho = 5.13$	$\rho = 5.42$	$\rho = 5.88$	$\rho = 6.16$
Color	Colorless	Colorless	Colorless	Light yellow
Crystal size (mm ³)	0.2 · 0.08 · 0.05	0.06 · 0.11 · 0.1	0.04 · 0.17 · 0.14	0.12 · 0.16 · 0.1
Crystal system, space group			Monoclinic, $P2_1/a$ (no.14)	
Measuring range	$3^\circ < 2\theta < 62^\circ$	$3^\circ < 2\theta < 62^\circ$	$3^\circ < 2\theta < 50^\circ$	$3^\circ < 2\theta < 56^\circ$
No. of measured reflections	6497	17492	12374	8122
No. of unique reflections, R_{merge}	1941; 0.11	1899; 0.12	1135; 0.19	1633; 0.18
No. of refined parameters			59	
Absorption coefficient (cm ⁻¹)	$\mu = 389.2$	$\mu = 427.5$	$\mu = 500.3$	$\mu = 544.6$
Final R -values				
$wR(F^2)$	0.115	0.121	0.140	0.154
$R(F)$ (all data)	0.046	0.044	0.076	0.090
$R(F)$ ($F^2 > 4\sigma F^2$)	0.040 (1733)	0.041 (1798)	0.062 (959)	0.063 (1198)
Largest difference peak and hole/e (10^6 pm ³)	+ 3.37/−3.53	+ 3.03/−3.53	+ 2.51/−3.40	+ 2.46/−2.16

parameters for all atoms. Due to the high absorption coefficients of all investigated crystals (see Table 1), a numerical absorption correction with the program HABITUS [10] was applied to all data sets. Final atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3.

Further details of the crystal structure analyses are deposited at the Fachinformationszentrum Karlsruhe,

Table 2

Atomic coordinates and equivalent isotropic displacement parameters (10^4 pm^2) for $\text{Hg}_3\text{S}_2[\text{ZrCl}_6]$ (I), $\text{Hg}_3\text{Se}_2[\text{ZrCl}_6]$ (III), $\text{Hg}_3\text{Se}_2[\text{HfCl}_6]$ (IV) and $\text{Hg}_3\text{Se}_2[\text{ZrBr}_6]$ (VI)

Atom	Compound	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Hg1	(I)	0	0.5	0	2.20(1)
Hg1	(III)	0	0.5	0	2.43(2)
Hg1	(IV)	0	0.5	0	2.81(4)
Hg1	(VI)	0	0.5	0	3.24(3)
Hg2	(I)	0.26166(2)	0.29713(4)	0.00958(5)	2.23(1)
Hg2	(III)	0.26235(3)	0.29580(5)	0.00732(6)	2.55(2)
Hg2	(IV)	0.26267(8)	0.2963(2)	0.0064(2)	2.99(3)
Hg2	(VI)	0.26318(6)	0.3015(2)	0.0087(2)	3.39(3)
Zr	(I)	0.5	0.5	0.5	1.34(2)
Zr	(III)	0.5	0.5	0.5	1.48(2)
Hf	(IV)	0.5	0.5	0.5	1.89(4)
Zr	(VI)	0.5	0.5	0.5	2.06(6)
S	(I)	0.1685(2)	0.5404(3)	0.1572(3)	1.73(3)
Se	(III)	0.1690(2)	0.5370(4)	0.1815(5)	2.45(7)
Se	(IV)	0.1684(2)	0.5421(3)	0.1643(4)	2.49(5)
Se	(VI)	0.16916(6)	0.5373(2)	0.1814(2)	1.92(2)
Cl1	(I)	0.4406(2)	0.6449(4)	0.1780(3)	2.74(4)
Cl1	(III)	0.4414(2)	0.6479(4)	0.1857(4)	3.03(4)
Cl1	(IV)	0.4418(5)	0.6482(9)	0.188(2)	3.0(2)
Br1	(VI)	0.4386(2)	0.6464(4)	0.1778(4)	3.46(6)
Cl2	(I)	0.5655(2)	0.7917(3)	0.6306(4)	2.55(4)
Cl2	(III)	0.5669(3)	0.7834(4)	0.6366(4)	2.70(4)
Cl2	(IV)	0.5666(6)	0.7814(9)	0.638(2)	3.2(2)
Br2	(VI)	0.5651(2)	0.8029(3)	0.6309(4)	3.15(5)
Cl3	(I)	0.3296(2)	0.5506(3)	0.6462(4)	2.51(4)
Cl3	(III)	0.3331(2)	0.5515(4)	0.6484(4)	2.67(4)
Cl3	(IV)	0.3339(6)	0.5518(9)	0.649(2)	2.8(1)
Br3	(VI)	0.3263(2)	0.5512(4)	0.6436(4)	3.09(5)

Table 3

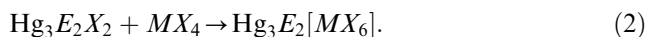
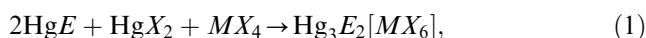
Selected bond lengths (pm) and angles (deg.) for $\text{Hg}_3\text{S}_2[\text{ZrCl}_6]$ (I), $\text{Hg}_3\text{Se}_2[\text{ZrCl}_6]$ (III), $\text{Hg}_3\text{Se}_2[\text{HfCl}_6]$ (IV) and $\text{Hg}_3\text{Se}_2[\text{ZrBr}_6]$ (VI)

Atoms	Distances/angles			
	(I)	(III)	(IV)	(VI)
<i>E</i> –Hg1	240.1(2)	251.68(9)	249.8(3)	253.1(2)
<i>E</i> –Hg2	238.1(2)	248.27(9)	249.1(4)	250.0(3)
<i>E</i> –Hg2 ^{II}	237.8(2)	248.55(9)	249.2(3)	250.4(3)
<i>M</i> –X1	247.3(2)	246.9(3)	244.3(7)	262.5(3)
<i>M</i> –X2	245.2(2)	246.4(3)	244.9(7)	261.0(3)
<i>M</i> –X3	245.9(2)	244.9(3)	245.2(7)	261.8(2)
X1– <i>M</i> –X2	91.15(8)	91.5(1)	91.2(3)	91.39(7)
X1– <i>M</i> –X3	90.82(7)	90.22(3)	90.8(3)	90.59(7)
X2– <i>M</i> –X3	91.82(7)	91.76(8)	91.3(3)	91.69(7)
Hg1– <i>E</i> –Hg2	101.04(7)	97.71(3)	97.9(1)	100.13(7)
Hg1– <i>E</i> –Hg2 ^{II}	104.36(7)	99.79(3)	99.9(1)	102.69(8)
Hg2– <i>E</i> –Hg2 ^{II}	101.64(7)	98.50(3)	98.1(2)	98.98(7)

D-77449 Eggenstein-Leopoldshafen, Germany, and can be obtained by quoting the literature citation, the names of the authors and the depository numbers CSD-412469 for $\text{Hg}_3\text{S}_2[\text{ZrCl}_6]$, CSD-412468 for $\text{Hg}_3\text{Se}_2[\text{ZrCl}_6]$, CSD-412466 for $\text{Hg}_3\text{Se}_2[\text{HfCl}_6]$, and CSD-412467 for $\text{Hg}_3\text{Se}_2[\text{ZrBr}_6]$ on request.

3. Results and discussion

The reaction of mercury chalcogenides HgS/HgSe with $\text{HgCl}_2/\text{HgBr}_2$ in the presence of zirconium or hafnium tetrahalide $\text{ZrCl}_4/\text{HfCl}_4/\text{ZrBr}_4$ under the conditions of the chemical vapor transport in closed ampoules yields a series of isotypic compounds of the general formula $\text{Hg}_3E_2[\text{MX}_6]$ in the form of colorless ($X=\text{Cl}$) and light-yellow ($X=\text{Br}$) air-sensitive crystals (Eq. (1)). The same result is achieved starting from the preformed Hg chalcogenide halides $\text{Hg}_3\text{S}_2\text{Cl}_2$ or $\text{Hg}_3\text{S}_2\text{Br}_2$ (Eq. (2))



The yields in these reactions do not exceed 40%. Even after prolonged heating only an equilibrium mixture still containing unreacted metal halide MX_4 is formed. Since the tetrahalide deposits together with the crystals of $\text{Hg}_3E_2[\text{MX}_6]$ in the colder part of the ampoules, only impure samples can be obtained by hand separation of the crystals. The visual similarity of the crystals of both compounds MX_4 and $\text{Hg}_3E_2[\text{MX}_6]$ makes this process difficult.

Crystals suitable for structure analyses could be obtained for $\text{Hg}_3\text{S}_2[\text{ZrCl}_6]$ (I), $\text{Hg}_3\text{Se}_2[\text{ZrCl}_6]$ (III), $\text{Hg}_3\text{Se}_2[\text{HfCl}_6]$ (IV), $\text{Hg}_3\text{Se}_2[\text{ZrBr}_6]$ (VI). $\text{Hg}_3\text{S}_2[\text{HfCl}_6]$ (II) and $\text{Hg}_3\text{S}_2[\text{ZrBr}_6]$ (V) could also be obtained in crystalline form. Twinning of the crystals could not be overcome with the result of high *R* values and inaccurate structural parameters in the structure determinations. The unit-cell determinations (lattice constants for II: $a = 1291.37(5)$, $b = 734.84(2)$, $c = 661.24(1)$ pm, $\beta = 91.78(1)^\circ$; for V: $a = 1350.99(6)$, $b = 756.79(3)$, $c = 701.97(3)$ pm, $\beta = 92.16(1)^\circ$) and the structure refinements, however, show unequivocally that these compounds belong to the same structure family.

The crystal structures are build of pyramidal EHg_3 groups ($E=\text{S}, \text{Se}$) linked via common Hg atoms to a sequence of layers and of discrete octahedral $[\text{MX}_6]^{2-}$ ions ($M=\text{Zr}, \text{Hf}$; $X=\text{Cl}, \text{Br}$) embedded between the layers (Fig. 1). The trigonal EHg_3 pyramids consist of a chalcogen atom in the apical position and three mercury atoms forming the basis. The Hg–*E* distances listed in Table 3 are almost identical with the respective bond lengths in $\text{Hg}_3\text{S}_2\text{Cl}_2$ (cubic phase, 241.6 pm [11]) and

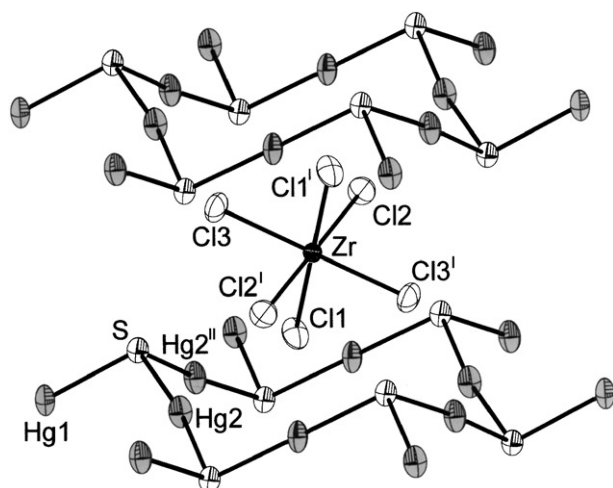


Fig. 1. A section of the structure of $\text{Hg}_3\text{S}_2[\text{ZrCl}_6](\text{I})$ as a representative of the structure type $\text{Hg}_3\text{E}_2[\text{MX}_6]$. Shown is the $[\text{ZrCl}_6]^{2-}$ ion and its coordination by two Hg_6S_6 ring fragments which are part of the two-dimensional $[\text{Hg}_3\text{S}_2]^{2+}$ cations. Displacement ellipsoids are scaled to enclose a probability density of 60%. Symmetry operations I: $-x+1, -y+1, -z+1$; II: $-x+1/2, y+1/2, -z$.

$\text{Hg}_3\text{Se}_2\text{Cl}_2$ (cubic phase, 250.8 pm [12]). The fact that substitution of X^- against a large complex ion as $[\text{MX}_6]^{2-}$ does not influence the $\text{Hg}-\text{E}$ bonds underlines the weakness of the $\text{Hg}-\text{X}$ bonds in the ternary phases $\text{Hg}_3\text{E}_2\text{X}_2$. The $\text{Hg}-\text{E}-\text{Hg}$ angles indicate the only slight distortion of the EHg_3 pyramids. In Fig. 2, a view along the c -axis shows the interconnection of the trigonal pyramids by the mercury atoms to infinite two-dimensional layers. The chalcogen atoms in the apical positions are pointing alternating upwards and downwards. Alternatively, the $[\text{Hg}_3\text{E}_2]^{2+}$ layers can be described as composed of condensed, 12-membered Hg_6E_6 rings in boat conformation with nearly linearly coordinated mercury atoms and a three-fold coordination of the chalcogen atoms. The structure of these layers reminds of the layers in the gray form of elemental arsenic. The layers are stacked perpendicular to the c -axis (Fig. 2). The monoclinic angle β causes a slight shift of each layer with respect to its two neighboring layers.

The MX_6 groups are of nearly regular octahedral shape ($M = \text{Zr}, \text{Hf}; X = \text{Cl}, \text{Br}$). The site symmetry $\bar{1}$ of the central group 4 metal atom causes three distinct $M-X$ distances (see Table 3), but only small differences are present. The $X-M-X$ angles show only small deviations from the ideal 90° and 180° , respectively. The hexahalogeno metalate anions are thus structurally closely related to the $[\text{MX}_6]^{2-}$ ions, for example, present in $[\text{SeCl}_3]_2[\text{MCl}_6]$ ($M = \text{Zr}, \text{Hf}$) [13] or $\text{In}_2[\text{ZrBr}_6]$ [14]. The $[\text{MX}_6]^{2-}$ ions are located above and underneath the centers of the Hg_6E_6 rings with two different orientations.

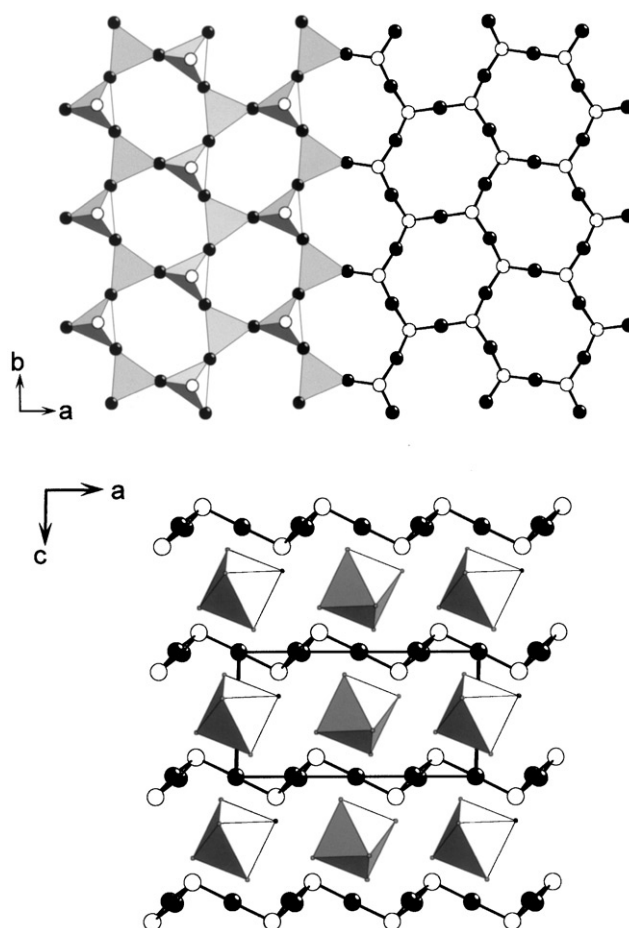


Fig. 2. View along the c -axis on one $[\text{Hg}_3\text{E}_2]^{2+}$ layer in the structure of $\text{Hg}_3\text{E}_2[\text{MX}_6]$ (top). On the left, the trigonal Hg_3E pyramids facing upwards and downwards are represented. On the right, the layer is shown in a ball and stick model with black circles for Hg and white circles for E . A view along the b -axis (bottom) shows the layered structure. The $[\text{MX}_6]^{2-}$ ions are shown as gray octahedra.

This arrangement of complex ions is closely related to the structure of $\text{Hg}_3\text{S}_2[\text{SiF}_6]$, which represents a higher symmetric congener [4]. $\text{Hg}_3\text{S}_2[\text{SiF}_6]$ is built of the same units as present in the $\text{Hg}_3\text{E}_2[\text{MX}_6]$ compounds: EHg_3 pyramid-forming layers and discrete octahedral $[\text{SiF}_6]^{2-}$ ions intercalated between them. The structure of the hexafluoro silicate is of higher symmetry and more regular, the $\text{Hg}-\text{S}$ distances and the $\text{S}-\text{Hg}-\text{S}$ angles in the Hg_3S pyramids are equal. As a consequence, the 12-membered Hg_6S_6 rings are regular, and a projection perpendicular to the stacking direction of the layers shows an undistorted hexagonal net. The $[\text{SiF}_6]^{2-}$ ions all have the same orientation with respect to the layers. Their shape is not regular octahedral. The site symmetry $3m$ of the Si atom causes three different $\text{F}-\text{Si}-\text{F}$ angles, whereas the $\text{Si}-\text{F}$ bonds are equal. The differences between the two structure types are apparently caused by the smaller size and the lower basicity of the

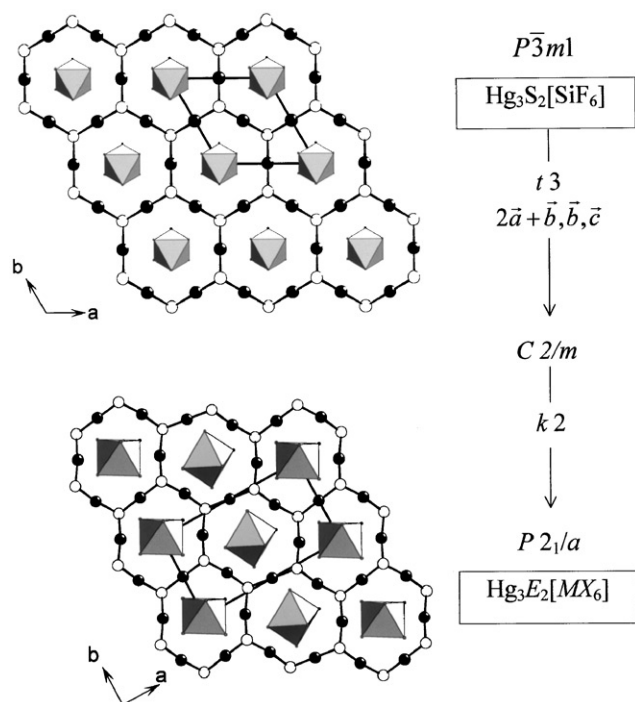


Fig. 3. Supergroup–subgroup relation between the structure of $\text{Hg}_3\text{S}_2[\text{SiF}_6]$ (top) and $\text{Hg}_3\text{E}_2[\text{MX}_6]$ (bottom). The symmetry relations are denoted in form of a *Bärnighausen tree* [15].

hexafluoro ion with respect to the hexachloro and hexabromo ions.

Between the structures of $\text{Hg}_3\text{E}_2[\text{MX}_6]$ and $\text{Hg}_3\text{S}_2[\text{SiF}_6]$, a supergroup–subgroup relation as shown in Fig. 3 can be formulated. Removing the three-fold axis and doubling of the unit cell according to the transformation $2\bar{a} + \bar{b}, \bar{b}, \bar{c}$ leads in a *translationengleich* reduction step of index 3 to the monoclinic space group $C2/m$. Removal of the lattice centering leads in a *klassengleich* transition of index 2 to the actual space group $P2_1/a$.

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