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Crystal chemistry of compounds containing mercury in low oxidation states

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Abstract. The published data are surveyed and a comparative crystal-chemical analysis is presented for the structures of compounds containing mercury in low oxidation states as cluster Hg_n groups with covalent Hg – Hg bonds. The geometry of compounds with Hg – Hg and Hg – X bonds (X = O, S, Se, N or Hal) is analysed and the types of coordination of mercury ions, the packing modes and the relationships between structural units are described. The crystallographic and crystal-chemical data for mercury compounds are given. The bibliography includes 124 references.

I. Introduction

It is known that mercury can exist not only in the oxidation state of +2 typical of Group II elements, but also in lower oxidation states which form polyatomic groups of the cluster type. These groups are found in inorganic complex compounds as well as in mercury-containing transition metal clusters. Diatomic groups (the so-called dumbbell-like groups), in which atoms of monovalent † mercury [1] are bound through a covalent bond and the Hg – Hg distances vary in the range of 2.5 – 2.6 Å, are most widespread. A large body of research of Hg(I) compounds confirmed the presence of the $(Hg_2)^{2+}$ pairs in the linear –X–Hg–Hg–X– fragments (X = O, N, S, Se or Hal), which contain two almost collinear *sp* bonds, as in the analogous –X–Hg–X– fragments in Hg(II) compounds. The $(Hg_2)^{2+}$ pairs were found for the first time in studies of mercurous halides Hg_2X_2 (X = F, Cl, Br or I). These pairs were also observed in approximately twenty minerals.[2] The Hg_3 'triangles', in which mercury exists in the formal oxidation state of +4/3 and the Hg – Hg distance is ~2.7 Å (in metallic mercury, the Hg – Hg distance is ~ 3 Å), are less abundant. A number of compounds contain linear systems of the Hg_n type (n = 3, 4, ∞) in which mercury atoms are bound to each other and exist in fractional oxidation states (+2/3, +1/2 or +1/3). As n increases, these compounds approximate metals in properties, and a pronounced correlation between the decrease in the charge on the mercury atom and the increase in the Hg – Hg distance (2.51 – 2.90 Å) is observed.

The crystal chemistry of mercury differs sharply from the crystal chemistry of its lighter analogues, *viz*., of zinc and cadmium. Unlike these metals, mercury can form polyatomic Hg_n^{x+} cations. Note that the $(Zn_2)^{2+}$ ion was found in a $Zn/ZnCl_2$ melt [1] and the $(Cd_2)^{2+}$ pair was detected in the $Cd_2(AlCl_4)_2$ compound (the distance between the cadmium atoms is 2.576 Å).[3]

There is no consensus of opinion as to the electronic structures not only of Hg_n^{x+} systems, but also of simple HgX_2 and Hg_2X_2 compounds. This is evidenced by numerous experimental and theoretical studies on the crystal and electronic structures of mercury-containing compounds and on the nature of bonding in these compounds. This heavy element with the closed shell electronic configuration $5d^{10}6s^2$ 'accumulates' all the factors, which hinder investigations of the electronic structures of its compounds by quantum-chemical methods. Thus, mercury is characterised by a large atomic number, the absence of unpaired electrons, the filled valence 5*d* and 6*s* orbitals, the presence of high-lying outer unoccupied 6*p* orbitals and a substantial influence of relativistic effects on the electronic state of the mercury atom and ions. Presently, factors, which contribute to the formation of Hg_n^{x+} systems, are not all revealed and the reasons for the changes in their sizes, the geometrical shape and the Hg – Hg distances are not understood.[4, 5]

II. Crystal structures of inorganic compounds containing $(Hg_2)^{2+}$ groups

More than 30 crystal structures of inorganic compounds containing $(Hg_2)^{2+}$ groups have been established. These structures belong to different types, *viz*., to molecular, layered or framework structures. The principal crystal-structural data for these com-

† Hereinafter, by monovalent mercury compounds are meant compounds containing $(Hg_2)^{2+}$ dimers.

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pounds are given in Table 1, in which the compounds are placed in order of increasing complexity of their structures, *viz*., beginning with simple molecular structures and ending with complicated framework structures.

A system containing the $(Hg_2)^{2+}$ pair and the oxygen atoms of two water molecules was found in the study[6] of the atomic arrangement in the $Hg_2(ClO_4)_2 \cdot 4H_2O$ compound both in aqueous solutions at various concentrations and in the solid state. In this system, the Hg—Hg and Hg—O distances are 2.50 and 2.14 Å, respectively, and the remaining Hg···O distances are larger than 2.70 Å. Apparently, the virtually linear $[H_2O-Hg-Hg-OH_2]^{2+}$ groups (the Hg—Hg—O angle is 178.1°) are present both in solution and in the crystal. It was demonstrated that a change in the concentration of the solutions has no effect on the Hg—Hg bond length. In addition, the metal–metal bonds in solutions (2.52 Å) and in the solid state (2.50 Å) differ only slightly. In the crystal structure, the $[H_2O-Hg-Hg-OH_2]^{2+}$ groups are located parallel to the *b* axis (Fig. 1). Two other water molecules and the oxygen atoms of the $[H_2O-Hg-Hg-OH_2]^{2+}$ cations and of the tetrahedral ClO_4^- anions are linked through hydrogen bonds (2.82 Å). In the study cited, mention was made of the existence of yet another hydrate, $Hg_2(ClO_4)_2 \cdot 2H_2O$, which also contains the $[H_2O-Hg-Hg-OH_2]^{2+}$ groups with the Hg—Hg and Hg—O distances of $\simeq$ 2.48 and $\simeq$ 2.10 Å, respectively.

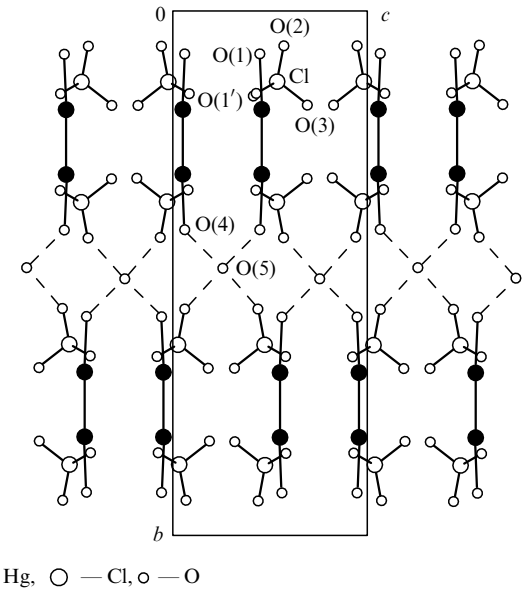


Figure 1. Projection of the crystal structure of $Hg_2(ClO_4)_2 \cdot 4H_2O$ onto the (100) plane. Hydrogen bonds are indicated by dashed lines.

Analogous linear groups were found in the structures of hydrates $Hg_2(NO_3)_2 \cdot 2H_2O$,[7,8] $Hg_2SiF_6 \cdot 2H_2O$ (see Ref. 9) and $Hg_2AlF_5 \cdot 2H_2O$.[10]

Two studies were devoted to the structure of $Hg_2(NO_3)_2 \cdot 2H_2O$.[7,8] Originally,[7] the coordination environment about the mercury atoms in the $(Hg_2)^{2+}$ pairs was described as a tetrahedron. The rather short distance between the mercury atom and the oxygen atom of the water molecule is indicative of the formation of the aqua $[H_2O-Hg-Hg-OH_2]^{2+}$ cations. In the crystal structure, the water molecules and the NO_3^- anions are linked through hydrogen bonds (2.29–2.60 Å). The structure refinement of $Hg_2(NO_3)_2 \cdot 2H_2O$[8] confirmed the existence of the aqua $[H_2O-Hg-Hg-OH_2]^{2+}$ cation. However, it was demonstrated that the coordination environment about the mercury atom is formed only by the two nearest neighbours, *viz*., by the mercury atom of the $(Hg_2)^{2+}$ pair and the oxygen atom of the water molecule. The remaining Hg···O distances vary from 2.68 to

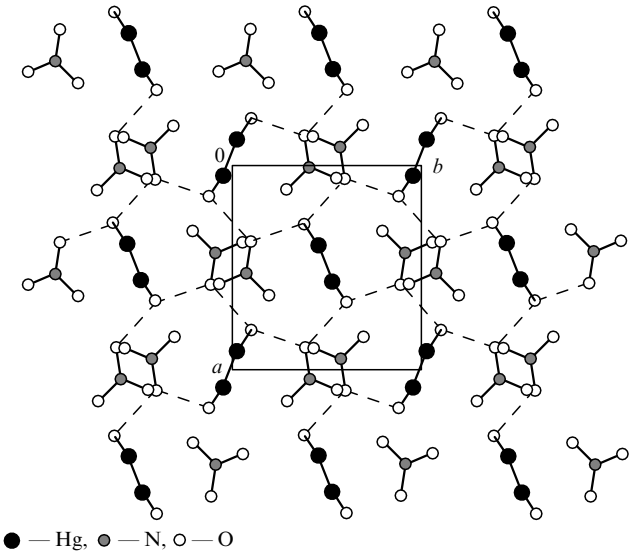


Figure 2. Herringbone molecular packing in the structure of $Hg_2(NO_3)_2 \cdot 2H_2O$.

3.03 Å. Two water molecules are linked to the same oxygen atom of the NO_3^- group through the hydrogen bonds between the H_2O molecules and the NO_3^- anion (2.68 and 2.70 Å) (Fig. 2). It should be noted that the Hg—Hg and Hg—O bond lengths in the $Hg_2(ClO_4)_2 \cdot 4H_2O$ and $Hg_2(NO_3)_2 \cdot 2H_2O$ compounds are virtually identical, but the $[H_2O-Hg-Hg-OH_2]^{2+}$ fragments in $Hg_2(NO_3)_2 \cdot 2H_2O$ deviate significantly from linearity (the Hg—Hg—O angle is 167.5°), which may be a consequence of the difference in the packing of these fragments in the crystal structures.

The structure of the $Hg_2SiF_6 \cdot 2H_2O$ compound was described as a ionic structure containing the slightly nonlinear aqua $[H_2O-Hg-Hg-OH_2]^{2+}$ cations (the Hg—Hg—O angle is 170.9°).[9] The mercury atoms each form contacts with three fluorine atoms of the octahedral SiF_6^{2-} anions. The Hg—F distances vary from 2.71 to 2.87 Å and the remaining distances are larger than 3 Å. In addition, there are hydrogen bonds between the fluorine atoms and the water molecules (F···O 2.58 and 2.65 Å).

The hydrogen bonds between the water molecules and the fluorine atoms (F···O 2.56–2.86 Å) are also of great importance in the $Hg_2AlF_5 \cdot 2H_2O$ compound.[10] These bonds stabilise the framework formed from *trans* chains of the AlF_6 octahedra parallel to the *c* axis. The quasi-linear $[H_2O-Hg-Hg-OH_2]^{2+}$ cations are located between the chains at different heights.

Therefore, the above-considered compounds containing the mercury atoms in the oxidation state of +1 and water molecules can be considered as within the ionic structures of the $[Hg(H_2O)]_2^{2+}$ cations.

Early investigations of the structures of halides with composition Hg_2X_2 (X = Cl, Br or I) have been devoted to the determination of the unit cell parameters and the atomic coordinates based on X-ray powder data.[3] More recently, the structures of Hg_2X_2 (X = F, Cl or Br) were refined based on single-crystal X-ray data.[11,12] The crystal structure of mercurous chloride Hg_2Cl_2 was determined also by neutron powder diffraction analysis.[13] It was confirmed that this compound has a linear molecular structure with the Hg—Hg and Hg—Cl distances of 2.5955 and 2.3622 Å, respectively. Longer intermolecular Hg···Cl contacts (3.2059 Å) were also found. The Cl···Cl distances between the adjacent linear Cl—Hg—Hg—Cl molecules along the [001] direction are 3.586 and 3.667 Å.

The molecular character of the structure and virtually linear —O—Hg—Hg—O— groups were found in the study of the crystal structure of $Hg_2(BrO_3)_2$.[14] The $(Hg_2)^{2+}$ pairs are located

Table 1. Crystallographic and crystal-chemical characteristics of low-valent mercury compounds.

Compound	Space group	Z	Unit cell parameters						V /Å^3	d_{calc} /g cm^{-3}	d_{exp}	Bond length /Å		The Hg – Hg – X angle [a]	Ref.
			a	b	c	α	β	γ				Hg – Hg	Hg – X [a]		
Inorganic monovalent mercury compounds															
$Hg_2(ClO_4)_2 \cdot 4H_2O$	*Imma*	4	7.59	20.59	7.55				1162.7	3.839	–	2.50	2.14	178.1	6
$Hg_2(NO_3)_2 \cdot 2H_2O$	$P2_1/n$	2	8.64	7.52	6.30		103.8		397.5	4.683	–	2.54	2.15, 2.40, 2.42	160	7
$Hg_2(NO_3)_2 \cdot 2H_2O$	$P2_1/n$	2	8.633(3)	7.506(4)	6.256(3)		103.8(1)		393.7	4.733	4.785	2.508	2.13 2.68 – 3.03	167.5	8
$Hg_2SiF_6 \cdot 2H_2O$	$P2_1/c$	2	5.642(1)	8.601(2)	8.922(2)		123.8(2)		355.9	5.41	5.37	2.495	2.20, 2.713 – 2.894	170.9	9
$Hg_2AlF_5 \cdot 2H_2O$	*I*4*cm*	4	9.353(5)	9.353(5)	7.241(6)				633.4	5.86	–	2.511	2.144 2.827 – 2.894	173.0	10
Hg_2Br_2 (kuzminite)	*I*4/*mmm*	2	4.663(1)	4.663(1)	11.133(2)				242.1	7.696	–	2.49	2.71, 3.32	180 (Hg – Hg – Br)	11
Hg_2F_2	*I*4/*mmm*	2	3.6700(4)	3.6700(4)	10.901(2)					9.93	–	2.51	2.133	180 (Hg – Hg – F)	12
Hg_2Cl_2 (calomel)	*I*4/*mmm*	2	4.4795(5)	4.4795(5)	10.9054(9)				218.83	7.162	–	2.5955	2.3622, 3.2059	180 (Hg – Hg – Cl)	13
$Hg_2(BrO_3)_2$	*C*2/*c*	4	18.806(7)	4.470(1)	8.595(2)		107.19(3)		690.2	6.32	6.20	2.507	2.16 2.69, 2.66	174.0	14
$HgReO_4$	$P2_1/c$	4	5.663(1)	5.070(1)	15.204(2)		110.17(1)		409.7	7.31	–	2.506	2.24 – 2.62	159.4	15
$Hg_2(NO_2)_2$	$P2_1/c$	2	4.4145(9)	10.333(2)	6.277(1)		108.83(1)		271.03	6.04	6.20	2.516	2.244	174.2	16
$Hg_2(NO_2)_2$	$P2_1/c$	2	4.435(1)	10.344(2)	6.301(2)		108.74(2)		273.7	5.99	–	2.520	2.224 2.577 – 2.955	173.3	17
$Hg_2(H_2PO_4)_2$	$P2_1/n$	2	6.0754(5)	14.5034(7)	4.7280(4)		92.172(7)		416.3	4.75	4.70	2.499	2.142, 2.514	167.2	18
$HgVO_3$	$P\bar{1}$	2	3.592(1)	4.752(1)	8.588(1)	88.32(1)	79.60(1)	89.30(1)	144.1	6.901	–	2.543	2.112 2.708 – 2.946	174.1	19
$Hg_2Mo_2O_7$	$P\bar{1}$	1	7.097(2)	7.144(2)	8.038(2)	65.89(1)	66.09(1)	166.45(1)	324.4	7.22	–	2.522	2.079, 2.139 2.735 – 3.112	167.3, 178.8	20
$Hg_2Mo_5O_{16}$	$P2_1/c$	2	9.139(1)	5.513(1)	14.289(2)		110.65(1)		673.7	5.604	–	2.474	2.208 2.553 – 3.113	152.7	21
$(Hg_2)_3(AsO_4)_2$	$P2_1/c$	2	8.73(2)	5.08(1)	15.64(3)		128.4(3)		543.6	9.06	9.05	2.535	2.16 – 2.23 2.42 – 2.71	146 – 157	23
Hg_2O_4	$P2/c$	2	6.2802(9)	4.4273(5)	8.367(2)		91.76		232.5	7.10	7.05	2.500	2.24, 2.49 – 2.93	165	24
Hg_2SeO_4	$P2/c$	2	6.3507(8)	4.5870(7)	8.499(2)		90.98		247.5	7.27	7.14	2.51	2.21, 2.50 – 2.90	160	24
$[(Hg_2)_2O(NO_3)](NO_3) \cdot \cdot HNO_3$	*Aba*2	8	11.222(8)	20.178(2)	9.354(2)				2118	6.306	6.30	2.502 – 2.513	2.12 – 2.31 2.46 – 2.96	145.9 – 173.3	27
$[(Hg_2)_5(OH)_4(NO_3)_2](NO_3)_4$	$P\bar{1}$	1	9.990(3)	9.091(4)	7.657(3)	94.05(3)	101.25(3)	109.75(3)	634.9	6.398	6.31	2.495 – 2.511	2.09 – 2.22 2.61 – 2.87	166.1 – 178.5	27
$Hg_2OH(NO_3)Hg_2(NO_3)_2$	*Cc*2*a*	8	20.171(5)	9.358(3)	11.217(3)				2117	6.31	6.30	2.499 – 2.505	2.142 – 2.364 2.488 – 2.733	140.5 – 170.8	29
$Hg_{10}(OH)_4(NO_3)_6$	$P\bar{1}$	1	9.994(5)	9.099(5)	7.659(2)	85.98(4)	78.70(3)	109.83(5)	635.5	6.39	6.20	2.488 – 2.505	2.052 – 2.266 2.602 – 2.966	165.9 – 178.8	30
$Hg_4(PO_4)(NO_3) \cdot H_2O$	$P2_1/n$	4	18.38(9)	8.258(3)	5.952(8)		91.2(1)		903.2	7.19	7.10	2.508 – 2.532	2.11 – 2.21 2.45 – 2.85	147.8 – 168.1	31
$AgHg_2PO_4$	*Pbam*	4	9.256(2)	8.614(2)	6.152(2)				–	–	–	2.608	2.224 – 2.348	101.2, 140.1, 142.9	32
$Hg_4OPb_2(NO_3)_6$	*Fd*3*m*	8	15.412	15.412	15.412				3660.8	5.823	–	2.458	2.108		33
$K_5Cs_5[(Hg_2)_2WO(H_2O) \cdot \cdot (AsW_9O_{53})_2]$	$P\bar{1}$	4	28.99(1)	18.82(1)	16.88(1)	78.49(1)	84.36(8)	78.25(6)	8818	4.86	4.90	2.446 – 2.545	2.16, 2.34	161.7	34
$Hg_4SbO_3(OH)_3$ (shakhovite)	*Im*	2	4.871(1)	15.098(3)	5.433(1)		98.86(2)		394.8	8.60	–	2.543	2.135, 2.160, 2.514 – 2.193	155.0, 166.3	35

Table 1 (continued).

Compound	Space group	Z	Unit cell parameters						V /Å^3	d_{calc} /g cm^{-3}	d_{exp}	Bond length /Å		The Hg–Hg–X angle [a]	Ref.
			a	b	c	α	β	γ				Hg–Hg	Hg–X [a]		
Hg_3OCl (poyarkovite)	$C2/c$	24	19.009(5)	9.018(4)	16.848(9)		110.81(3)		2696	9.643	–	2.503 – 2.565	1.96 – 2.30, 2.60 2.818 – 3.043 (Cl)	137.8 – 173.2	36
$(Hg_2)_3O_2Cl_2H$ (eglestonite)	$Ia3d$	16	16.036(3)	16.036(3)	16.036(3)				4123.7	8.652	–	2.516	2.165 3.010 – 3.095 (Cl)	162.7	37
Hg_2TeO_3 (magnolite)	$Pbm2$	2	5.958(1)	10.576(2)	3.749(1)				236.2	8.108	–	2.532	2.06, 2.69 – 3.00	167.0	38
$Hg_6Si_2O_7$ (edgarbaileyite)	$C2/m$	2	11.755(3)	7.678(2)	5.991(2)		111.73(3)		502.3	9.10	–	2.522, 2.524	2.12, 2.21 2.41 – 2.86	177.2, 164.9	39
$(Hg_2)_8(Ni,Mg)_6(CO_3)_{12}(OH)_{12}-$ $-(H_3O)_8(H_2O)_x$ ($x \sim 3$) (szymanskiite)	$P6_3$	1	17.3984(7)	17.3984(7)	6.0078(4)			120	1574.9	4.86	–	2.494, 2.513	2.099 – 2.144 2.34 – 2.44	136.3 – 175.2	40
Mixed-valence mercury compounds															
Hg_2OI	$C2/c$	8	17.603(8)	6.981(5)	6.701(5)		101.61(2)		807	8.96	–	2.534	2.141	174.6	46
$[Hg_2(OHg)_2](NO_3)_2$	$P2_1/c$	2	5.532(3)	6.659(2)	11.578(5)		98.84(3)		421.4	7.552	7.52	2.510	2.16	177.9	27
$Hg_4O_2(NO_3)_2$	$P2_1/a$	2	11.580(2)	6.664(1)	5.533(1)		98.82(1)		422	7.54	7.5	2.510	2.136	178.1	48
$Hg_8O_4Br_3$	$P2_1/n$	4	6.8554(9)	6.3033(9)	31.093(3)		96.09(1)		1336	9.49	–	2.517 – 2.557	2.10 – 2.24	165.1 – 172.4	49
Hg_2ReO_5	$P\bar{1}$	4	7.952(2)	8.948(2)	9.015(2)	114.11(1)	101.64(2)	91.19(2)	569.7	7.78	–	2.521	2.135, 2.143	170.4, 173.1	15
$Hg_5Re_2O_{10}$ (I)	$P2_1/b$	2	6.401(5)	7.981(5)	11.538(7)		98.87(19)		582.4	8.755	–	2.546	2.14, 2.19	164.0, 173.9	52
$Hg_5Re_2O_{10}$ (II)	$P2_1/c$	4	8.615(1)	12.009(2)	12.039(2)		97.15(1)		1235.8	8.25	–	2.520, 2.508	2.102 – 2.258	145.7 – 177.9	53
Hg_2VO_4	$P2_1/n$	8	3.673(1)	16.503(1)	14.255(1)		89.99(1)		864.1	7.934	–	2.536	2.20	153, 173	19
$Hg_9P_5I_6$	$P2_1/c$	4	13.112(5)	12.486(2)	17.031(3)		119.90(2)		2419.0	7.472	–	2.541	2.452 (Hg–P) 3.568 – 3.675 (Hg–I)	168.7 (Hg–Hg–P)	55
$Hg_5CrO_5S_2$ (deanesmithite)	$P\bar{1}$	2	8.1287(8)	9.4916(7)	6.8940(4)	100.36(1)	110.16(1)	82.98(1)	490.13	8.14	–	2.536	2.11, 2.352 – 2.442 (Hg–S)	171.3 (Hg–Hg–S) 167.6	57
Hg_5CrO_6 (wattersite)	$C2/c$	4	11.274(2)	11.669(2)	6.603(1)		98.19(2)		859.8	8.891	–	2.526	2.10 – 2.16	153.3, 169.5	58
$HgHg_6[Cl(OH)]_2O_3$ (hanawaltite)	$Pbma$	4	11.777(2)	13.891(3)	6.460(1)				1056.9	9.51	–	2.526, 2.56	1.93 – 2.30	175.4, 177.0	59
$Hg_4O_2Cl_2$ (*terlinguaite*)	$C2/c$	4	11.953(4)	5.904(3)	9.466(4)		105.59(6)		643	9.35	9.40	2.703, 2.587(Cl)	2.234, 2.462,	60 (Hg–Hg–Hg)	44
$Hg_3(AsO_4)Cl$ (kuznetsovite)	$P2_13$	4	8.379(3)						588.3	8.763	–	2.675	2.17 – 2.28	60 (Hg–Hg–Hg)	60
$Hg_9(AsO_4)_4$	$R3c$	6	16.603(1)	–	10.830(2)				2585.4	9.038	–	2.662 – 2.696	2.142 – 2.343 (Hg–Hg–Hg)	59.5 – 60.8	
Compounds containing $(Hg_3)^{2+}$ groups and Hg_n chains															
$Hg_3(AsF_6)_2$, $(Hg_3)^{2+}$ group	$P2_1/c$	2	5.981(5)	8.551(6)	11.282(10)		91.16(7)		577.1	5.67	–	2.552	2.38 2.83 – 2.96	180 (Hg–Hg–Hg) 168.9 (Hg–Hg–F)	63
$Hg_3(AlCl_4)_2$, $(Hg_3)^{2+}$ group	$P2_1/c$	4	7.1321(2)	15.0468(3)	14.1771(4)		99.05(3)		1502.5	4.16	3.95	2.551 2.562	2.517, 2.562 (Cl)	174.4 (Hg–Hg–Hg) 172.8, 176.6 (Hg–Hg–Cl)	66
$Hg_3(NbF_5)_2(SO_4)$, $(Hg_3)^{2+}$ group	$Fdd2$	8	18.068(6)	15.734(5)	9.176(4)				2608.6	5.49	5.467	2.562	2.276 (O) 2.809 – 2.990 (F)	166.6 (Hg–Hg–Hg) 174.8 (Hg–Hg–F)	67
$Hg_3(TaF_5)_2(SO_4)$, $(Hg_3)^{2+}$ group	$Fdd2$	8	18.078(7)	15.705(4)	9.153(2)				2599	6.388	6.387	2.554	2.27 (O) 2.76 – 3.00 (F)	166.2 (Hg–Hg–Hg)	67
$Hg_4(Ta_2F_{11})_2$, $(Hg_n)^{2+}$ chain	$I2/c$	4	18.556(8)	7.528(3)	14.714(8)		91.72(4)		2054	–	6.285	2.593, 2.630 3.033 (Hg···Hg)	2.74 – 2.82 2.97 – 3.23	177.2 (Hg–Hg–Hg) 165.1 (Hg–Hg–F)	67
$Hg_4(AsF_6)_2$, $(Hg_n)^{2+}$ chain	$P2_1/c$	2	5.489(2)	11.633(4)	9.85(6)		92.20(4)		628.5	6.24	–	2.588, 2.620 2.985	2.71 – 2.95 3.06 – 3.34 (Hg···Hg)	177.3 (Hg–Hg–Hg) 141.3 (Hg–Hg–F)	68

Table 1 (continued).

Compound	Space group	Z	Unit cell parameters						V /Å^3	d_{calc} /g cm^{-3}	d_{exp}	Bond length /Å		The Hg−Hg−X angle [a]	Ref.
			a	b	c	α	β	γ				Hg−Hg	Hg−X [a]		
$Hg_{2.86}AsF_6$, $(Hg_n)^{2+}$ chain	$I4_1/amd$	4	7.538(4)	7.538(4)	12.339(5)				701.1	7.224	–	2.64	2.99	180 (Hg−Hg−Hg)	70
$Hg_{2.86}(AsF_6)_{0.953}$, $(Hg_n)^{2+}$ chain	$I4_1/amd$	4	7.549(5)	7.549(5)	12.390(9)				706.1	7.04	7.06	3.24 (Hg···Hg)	2.87 2.98	180 (Hg−Hg−Hg)	71
$Hg_{3-\delta}SbF_6$ [δ = 0.10(2)], $(Hg_n)^{2+}$ chain	$I4_1/amd$	4	7.711(2)	7.711(2)	12.641(2)				751.6	7.22	–	2.66 3.22 (Hg···Hg)	2.86, 2.98	–	72
$Hg_{3-\delta}TaF_6$ [δ = 0.116(4)], $(Hg_n)^{2+}$ chain	$I4_1/amd$	4	7.711(1)	7.711(1)	12.714(2)				756.0	7.68	–	2.67 3.239 (Hg···Hg)	2.86, 2.983	–	73
$Hg_{3-\delta}NbF_6$ [δ = 0.119(2)], $(Hg_n)^{2+}$ chain	$I4_1/amd$	4	7.692(1)	7.692(1)	12.679(2)				750.2	6.95	–	2.67 3.222 (Hg···Hg)	2.86, 2.97	–	73
$Hg_{3-\delta}SbF_6$ [δ = 0.134(1)], $(Hg_n)^{2+}$ chain	$I4_1/amd$	4	7.655(1)	7.655(1)	12.558(1)				735.9	7.314	–	2.67 3.210 (Hg···Hg)	2.81, 2.956	–	74
$Hg_{3-\delta}TaF_6$ [δ = 0.142(2)], $(Hg_n)^{2+}$ chain	$I4_1/amd$	4	7.634(1)	7.634(1)	12.610(1)				734.9	7.844	–	2.67 2.937 (Hg···Hg)	2.81, 2.937	–	74
Hg_3NbF_6, layer $(Hg)_n$	$P\bar{3}\ 1m$	1	5.02(1)	5.021(1)	7.68(7)			120	167.6	8.0	–	2.90	3.2	–	75
Monovalent mercury compounds with organic ligands															
$Hg_2(L^1)_2(ClO_4)_2$	$P2_1/c$	2	5.509(5)	15.110(10)	11.630(10)		98.1(1)		958	2.80	–	2.498	2.16 (N)	176.0	79
$Hg_2(L^2)_2(ClO_4)_2$	$C2/m$	8	16.49(2)	22.92(4)	5.04(1)		92.4(1)		1904	2.89	2.81	2.487	2.21 (N)	167.4	80
$Hg_2(L^3)_2(ClO_4)_2$	$P2_1/n$	2	18.639(3)	5.164(1)	11.224(1)		105.95(1)		1038.6	2.75	2.65	2.511	2.03 (N)	174.4	81
$Hg_2(L^4)_2(ClO_4)_2$	$I2/m$	2	10.629(1)	16.841(1)	7.142(1)		99.06(2)		1262.5	2.52	2.51	2.5177	2.15 (N)	180	82
$Hg_2(L^5)_2(ClO_4)_2 \cdot H_2O$	$P2_1/n$	4	15.913	25.794	5.979		95.42		2443.2	2.738	–	2.501	2.16, 2.21 (N)	162.8, 171.5	83
$Hg_2(L^6)(ClO_4)_2$	$P\bar{1}$	2	10.206(2)	12.006(8)	14.411(6)	69.60(5)	83.04(13)	66.53(4)	1518.02	2.294	2.31	2.506	2.20 (N); 2.63, 2.69 (O)	170.3, 172.9	84
$Hg_2(L^7)_4(ClO_4)_2$	$P2_1/c$	2	11.729(1)	10.896(1)	18.392(2)		96.20(1)		2336.7	1.78	1.77	2.5084	2.227 (N) 2.476 (N)	153.9, 118.4 87.5 (N−Hg−N)	85
$Hg_2(L^8)_4(ClO_4)_2$	$P\bar{1}$	2	8.68(1)	12.76(2)	14.00(2)	115.2(1)	85.8(1)	97.5(1)	1390	2.34	2.35	2.523	2.19 (O) 2.34 – 2.56	105.9 – 159.9	87
$Hg_2(Ph_2Se)_4(ClO_4)_2$ (yellow form)	$P2_1/n$	2	13.910(8)	14.575(9)	12.109(6)		92.60		2452	2.08	2.27	2.5579	2.701, 2.802 (Se) 2.705 (O)	116.4, 141.1 (Hg−Hg−Se) 103.3 (Hg−Hg−O) 100.56 (Se−Hg−Se)	88
$Hg_2(Ph_2Se)_4(ClO_4)_2$ (red form)	$P2_1/n$	2	11.609	14.462	14.391		98.20		2392	2.13	2.27	2.553	2.653, 2.919 (Se) 2.626 (O)	104.4, 152.0 (Hg−Hg−Se) 109.6 (Hg−Hg−O) 102.7 (Se−Hg−Se)	89
$Hg_2(Ph_3PO)_6(ClO_4)_2$	$P\bar{1}$	1	12.55(1)	14.47(2)	16.05(2)	120.0(1)	82.3(1)	95.2(1)	2499	1.51	1.50	2.522	2.29 – 2.43 (O)	116.0 – 140.0 79.4 – 86.4 (O−Hg−O)	90
$Hg_2Phen(NO_3)_2$	$P\bar{1}$	2	6.83(2)	10.55(3)	10.58(3)	98.6(1)	93.0(1)	97.6(1)	744	3.15	3.04	2.516	2.30 – 2.48 (N) 2.227 – 2.590 (O)	131.7, 136.7, 171.3	91
$Hg_2(L^9)_2(NO_3)_2$	$C2/c$	4	10.628(9)	10.219(8)	18.236(15)		100.35(6)		1948.34	2.67	2.61	2.551	2.168 (N)	164.4	92
$Hg_2(L^{10})_2(NO_3)_2$	$C2/c$	4	26.969(4)	5.273(1)	16.956(4)		100.89(1)		2368.0	2.56	–	2.517	2.192 (N)	160.5	93
$Hg_2(L^{11})_2(NO_3)_2$	$P2/c$	2	8.6819(5)	5.3696(6)	19.7645(8)		95.138(12)		917.74	2.70	2.75	2.518	2.233 (N), 2.658 (O)	164.3, 113.9	94

Table 1 (continued).

Compound	Space group	Z	Unit cell parameters						V /Å^3	d_{calc}	d_{exp}	Bond length /Å		The Hg–Hg–X angle [a]	Ref.
			a	b	c	α	β	γ		/g cm^{-3}		Hg–Hg	Hg–X [a]		
$Hg_2(L^{12})_2(NO_3)_2$	$P\bar{1}$	2	5.4878(1)	8.4085(1)	9.6062(1)	92.599(3)	94.763(3)	89.614(3)	441.283	2.865	–	2.524	2.209 (N)	169.5	95
$Hg_2(L^{13})_2(NO_3)_2$	$P2/c$	4	6.970(5)	15.205(8)	11.185(8)		96.0(6)		1178.9	3.67	3.55	2.541	2.496, 2.584 (S) 2.516 (O)	173.5, 138.7	96
$[Hg_2(L^{14})_2]_2(NO_3)_2$	$P2/n$	2	11.755(9)	10.798(8)	8.760(8)		110.74(4)		1039.86	1.972	–	2.549	2.469, 2.489 (S) 2.636, 2.652 (O)	162.0, 163.3 101.3, 113.0	97
$Hg_2(L^{15})_2(H_2O)_2$	$C2/c$	4	9.989(9)	11.788(9)	13.527(13)		94.350(9)		1588.22	3.151	–	2.494	2.203 (N), 2.621 (O)	165.7	98
$Hg_2(L^{16})_2$	$C2/c$	4	23.624(4)	6.057(9)	14.857(3)		126.23(7)		1714.86	2.89	2.80	2.500	2.179 (N)	170.7	99
$Hg_2(L^{17})_2$	$P\bar{1}$	1	9.311(9)	7.347(3)	6.985(3)	114.80(15)	92.69(4)	86.41(7)	432.80	2.86	2.80	2.515	2.187 (N), 2.68 (O)	169.6, 107.3	99
$Hg_2(L^{17})_2(H_2O)_2$	$P2/n$	2	11.944(3)	7.588(2)	10.345(4)		105.44(6)		903.74	2.87	2.80	2.522	2.201 (N) 2.711, 2.715 (O)	172.8 89.7, 107.1	99
$Hg_2(L^{18})_2$	$C2/c$	8	26.330(20)	6.254(2)	12.90(10)		116.94(3)		1893.4	3.96	4.03	2.519	2.08, 2.16 (O)	171. 175	100
$Hg_2(L^{19})_2$	$P\bar{1}$	1	5.038(1)	5.970(1)	15.774(6)	80.77(2)	86.42(2)	84.38(2)	465.5	3.151	3.12	2.514	2.13 (O)	173.9	101
$Hg_2(CF_3CO_2)_2$	$C2/c$	4	14.866(5)	9.337(5)	8.230(5)		124.4(2)		943.8	4.412	4.391	2.505	2.14 (O)	166.6	102
$Hg_2[C(CN)_3]_2$	$P\bar{1}$	2	5.2794(1)	9.9297(1)	11.3376(2)	71.004(4)	76.459(2)	74.601(4)	534.647	3.611	–	2.506	2.287, 2.508 (N)	123.9, 121.3 123.0 – 140.0	103
$Hg_2(C_7NH_4)_2$	$P2_1/n$	2	9.9193(1)	5.6912(2)	13.3806(1)		92.544(2)		754.63	3.007	–	2.503	2.207 – 2.560 (N)	162.2, 116.5	104
$Hg_2(L^{20})_2(AlCl_4)_2 \cdot C_7H_8$	$P2_1/c$	4	21.160(10)	10.951(7)	18.80(10)		104.9(1)		4209.9	1.823	–	2.515	2.416, 2.672 (C)	–	105
Mercury-containing transition metal clusters															
$Hg_2Co_2[N(C_2H_4PPh_2)]_3 \cdot THF$	$P\bar{1}$	2	25.691(9)	13.387(5)	13.471(4)	119.56(8)	97.51(8)	87.25(7)	3994.48	1.578	–	2.651	2.429, 2.444		106
$\{Hg_2Pt_6[(Ph_2P)_2(CH_2)_6]_3 - -(C_8H_9NC)_6\} \cdot 2(C_6H_6)$	$C2/c$	4	56.86(8)	15.120(8)	31.01(3)		141.29(6)		16673	1.545	–	2.872 (Pt – Pt) 2.656 – 2.672	2.878 – 2.993		107
$[(Ph_3P)_2N]_2[Hg_2Os_{18}(CO)_{20}C_2]$	$P\bar{1}$	1	18.711(4)	16.379(3)	11.724(2)	111.242(2)	84.284(1)	105.994(2)	3220.08	3.147	–	2.744 (Os – Os) 2.743 – 3.038	2.636 – 2.907		108
$[(Ph_3P)_2N]_4[Hg_2Os_{18}(CO)_{42}C_2] \cdot \cdot CH_2Cl_2$	$P\bar{1}$	1	19.121(2)	16.638(4)	17.676(4)	89.23(2)	117.24(2)	94.03(2)	5053.91	2.326	–	2.820 (Os – Os) 2.748 – 3.092	2.474 – 2.898		109
$\{Hg_3[(Ph_2P)_2CH_2]_3\}(SO_4)_2 \cdot 1.5H_2O$	$P2_1/n$	4	15.069(2)	24.025(2)	22.405(2)		93.88(1)		8092.8	1.620	–	2.764 – 2.802	–		110
$[(Ph_3P)_2N]_2[Hg_3Ru_{18}C_2(CO)_{42}] \cdot \cdot CH_2Cl_2$	$P\bar{1}$	1	19.042(4)	15.729(3)	15.197(3)	115.59(2)	68.51(2)	115.46(2)	2983.18	2.66	–	2.919 – 2.934 2.733 – 3.010 (Ru – Ru)	2.640 – 2.734		111
$(C_{36}H_{30}NP_2)_2[Hg_3Os_9(CO)_{21}C_2] \cdot \cdot CH_2Cl_2$	$P\bar{1}$	1	19.022(4)	15.737(3)	15.205(3)	115.66(2)	68.32(2)	115.45(3)	3609.39	2.910	–	2.919, 2,931	2.678 – 2.762		112
$Hg_2Ag[(Ph_2P)_2CH_2]_3(CF_3SO_3)_3$	$P2_1/n$	4	15.256(3)	28.028(8)	21.863(3)		92.14(1)		9342	1.500	–	2.660	2.805, 2.853		114
$[Nb(\eta\text{-}C_5H_5)_2\{HgS_2CN(C_2H_5)_2\}_3]$	$P2_1/n$	4	12.302(10)	18.385(11)	16.077(5)		108.18(5)		3454.66	2.441	–	2.901, 2.883	2.777 – 2.808		115
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2Hg]_4$	$I\bar{4}$	2	15.959(2)	15.959(2)	7.683(1)		–		1956.8	2.64	–	2.888	2.640		116
$[(\eta^5\text{-}C_5H_5Re(CO)_2Hg]_4$	$C2/c$	8	20.036(14)	16.143(8)	22.111(13)		78.66(5)		–	3.85	–	2.92	2.74		117
$[(C_{12}H_{36})_3Rh]_4Hg_6$	$Ccmm$	4	12.909(2)	25.274(4)	25.176(4)		–		8213.9	2.05	–	3.131 – 3.149	2.690 – 2.724		118
$[(C_8H_{18}P)_2Pt]_4Hg_6$	$C2/c$	4	12.738(3)	48.692(6)	16.602(3)		95.16(2)		10255.47	2.037	–	3.081 – 3.274	2.671 – 2.876		119
$[Hg_9Co_6(CO)_{18}] \cdot 2(C_3H_6O)$	$P2_1/c$	4	14.341(6)	21.024(6)	18.543(9)		94.50(4)		5574	3.11	–	3.066 – 3.216	2.521 – 2.609		120

Note. Samples of natural and synthetic (italicised) minerals were studied; the unit cell parameters a, b and c are given in Å, the angles α, β, γ and Hg–Hg–X are given in deg.

[a] For inorganic monovalent mercury compounds, mixed-valence mercury compounds and compounds containing $(Hg_3)^{2+}$ groups and Hg_n chains X = O or Hal; for monovalent mercury compounds with organic ligands, X = N, O, Se or S; for mercury-containing transition metal clusters, X = Hg, Pt, Os or Ru.

nearly parallel to the *a* axis. The distances between the nearest pairs are 4.5 Å. The Hg—O distance in the —O—Hg—Hg—O— group is 2.16 Å. In addition, there are Hg···O distances (2.66 and 2.69 Å). Taking into account the latter contacts, the coordination environment about the mercury atoms can be described as a distorted tetrahedron. The $Hg_2(BrO_3)_2$ molecules are linked in linear chains along the *c* axis through weak O···O contacts (2.66 Å). The rows of the mercury pairs alternate with double rows of the BrO_3^- anions along the *a* axis (Fig. 3). The effect of the mercury atoms on the BrO_3^- groups consists in the increase in the distance between the bromine atom and the oxygen atom bound to the mercury pair. This distance is 1.76 Å, whereas two other Br—O bond lengths are 1.64 and 1.65 Å.

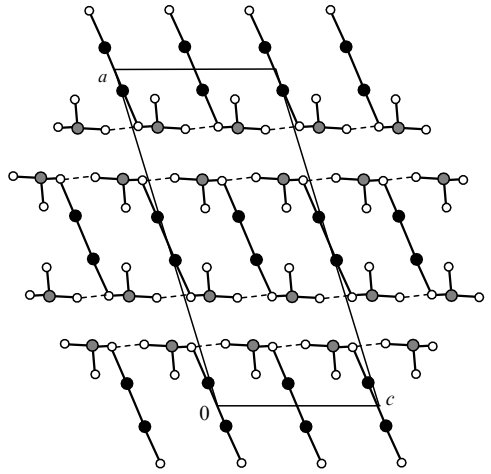


Figure 3. Projection of the crystal structure of $Hg_2(BrO_3)_2$ onto the (010) plane. The O···O contacts are indicated by dashed lines.

The crystal structure of $HgReO_4$ consists of discrete ($O_3Re—O—Hg—Hg—O—ReO_3$) groups, which are substantially nonlinear (the Hg—Hg—O angle is 159.4°), apparently, due to the type of the molecular packing in the monoclinic unit cell.[15] The mercury atoms each form contacts with the oxygen atoms of other structural units (the distances are larger than 2.49 Å) along with the short Hg—O bonds.

The virtually linear groups were also found in the first stucturally studied monovalent mercury nitride, $Hg_2(NO_2)_2$, consisting of the planar centrosymmetrical molecular $NO_2—Hg—Hg—NO_2$ groups.[16] The nonbonded Hg···O interactions (2.84 and 2.93 Å) are analogous to those found by Grdenic.[7] Taking into consideration these contacts, the coordination number of the mercury atom increases to 4. In the crystal structure of $Hg_2(NO_2)_2$, the molecules are packed in a herringbone fashion.[7,8] The structure of this compound was also studied by Ohba and coworkers.[17] In this study, the Hg···O bond (2.577 Å) was found along with the Hg—O (2.24 Å) bond, *i.e.*, both oxygen atoms of the NO_2^- group are bound to the mercury atoms of the $(Hg—Hg)^{2+}$ cations to form a planar centrosymmetrical molecule. In addition, Hg···O contacts (2.826 Å) between the adjacent molecules were revealed. The authors believed that the yellow colour of the crystals is associated with the bridging function of the $(Hg_2)^{2+}$ pairs.

A rather short Hg—Hg distance (2.499 Å) was observed in the structure of $Hg_2(H_2PO_4)_2$.[18] Each mercury atom has an oxygen atom as the nearest neighbour at a distance of 2.14 Å. The —O—Hg—Hg—O— fragment is nonlinear (the Hg—Hg—O angle is 167.2°). The distances between the mercury atom and the remaining oxygen atoms are larger than 2.5 Å. The structure of the complex consists of the discrete $Hg_2(H_2PO_4)_2$ molecules linked in a three-dimensional framework *via* hydrogen bonds (O···O 2.52–2.79 Å). The herringbone molecular packing in the crystal of the complex is analogous to those observed in anhydrous $Hg_2(NO_2)_2$ (see Refs 16 and 17) and its dihydrate $Hg_2(NO_2)_2 \cdot 2H_2O$.[8]

What the crystal structures of the two known mercurous vanadates, *viz*., $HgVO_3$ and the mixed-valence Hg_2VO_4, have in common is a distorted five-vertex coordination polyhedron about the vanadium formed by the oxygen atoms.[19] In both structures, the polyhedra of the vanadium atoms are linked *via* shared edges to form infinite $[(VO_3)^-]_n$ chains. In the structure of $HgVO_3$, these chains are linked through the $(Hg_2)_2^{2+}$ pairs in two-dimensional corrugated infinite $(Hg_2)_n^{2+}[(VO_3)^-]_{2n}$ layers, which are linked *via* weak interlayer Hg···O contacts (2.71–2.95 Å), unlike the mixed-valence Hg_2VO_4 compound, in which the $[(VO_3)^-]_n$ chains do not form strong bonds with the mercury atoms.

Only three mercury molybdates were structurally characterised. The compound $HgMoO_4$ contains the divalent mercury atom. The $Hg_2Mo_2O_7$ and $Hg_2Mo_5O_{16}$ polymolybdates contain the $(Hg_2)^{2+}$ ions. The layered structures of $Hg_2Mo_2O_7$ (see Ref. 20) and $Hg_2Mo_5O_{16}$ (see Ref. 21) are based on the MoO_4 tetrahedra linked in Mo_2O_7 groups and Mo_5O_{16} fragments, respectively. The coordination environment about the molybdenum atoms is a distorted octahedron. In both compounds, the Mo octahedra are linked in two-dimensional infinite layers *via* shared vertices and edges. The layers are separated by the $(Hg_2)^{2+}$ pairs (Fig. 4). In the structure of $Hg_2Mo_2O_7$, the Hg—Hg and Hg—O distances have standard values, whereas the Hg—Hg bond in $Hg_2Mo_5O_{16}$ is rather short (2.474 Å) and the —O—Hg—Hg—O— fragments deviate significantly from linearity (the Hg—Hg—O angle is 152.7°). Noteworthy is the similarity of the structures of $Hg_2Mo_5O_{16}$ and $Cs_2Mo_5O_{16}$.[22]

In the crystal structure of the synthetic analogue of the mineral chursinite $(Hg_2)_3(AsO_4)_2$ (see Ref. 23), the $(Hg_2)^{2+}$ cations and the AsO_4^{3-} anions are packed in such a manner that three of the four oxygen atoms of the AsO_4^{3-} groups are bound to three different mercury pairs (the Hg—O distances are 2.16, 2.22 and 2.23 Å) to form puckered layers. The fourth oxygen atom is bound to three mercury atoms of the adjacent layer (the Hg···O distances are 2.48, 2.46 and 2.71 Å) and has a distorted tetrahedral coordination, the As—O distance with this oxygen atom (1.78 Å) being larger than the remaining three As—O distances (the average value is 1.68 Å). These characteristic groups are linked to each other along the *a* axis through Hg···O contacts (2.68 and 2.42 Å) and along the *c* axis through Hg···O contacts (2.47 Å). Taking into account all interactions, the structure of $(Hg_2)_3(AsO_4)_2$ can be considered as a three-dimensional framework (Fig. 5). It should be noted that the —O—Hg—Hg—O— fragments are substantially nonlinear (the Hg—Hg—O angles are 146–157°).

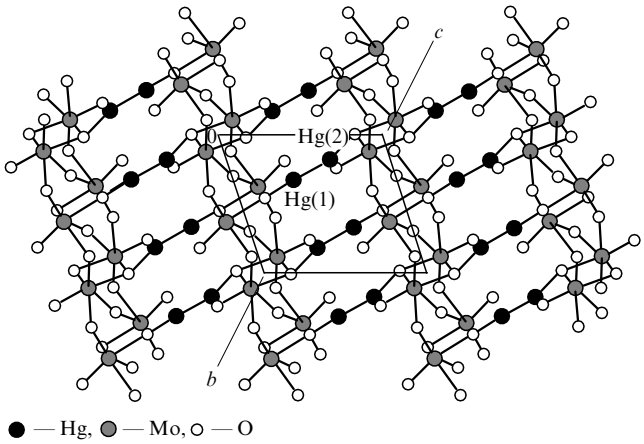


Figure 4. Crystal structure of $Hg_2Mo_2O_7$.

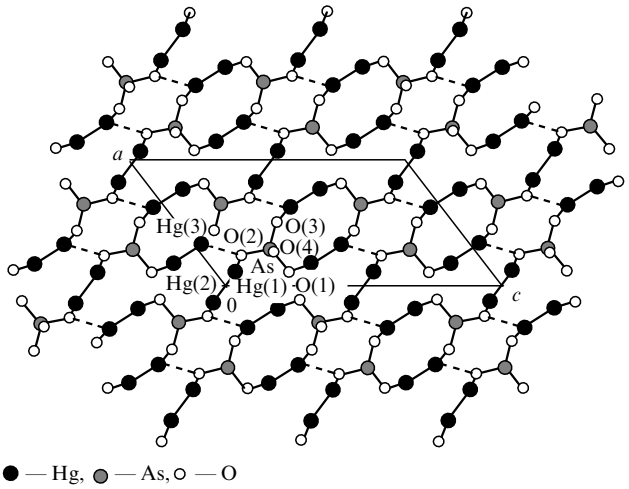


Figure 5. Projection of the crystal structure of $(Hg_2)_3(AsO_4)_2$ onto the (010) plane. The Hg···O contacts are indicated by dashed lines.

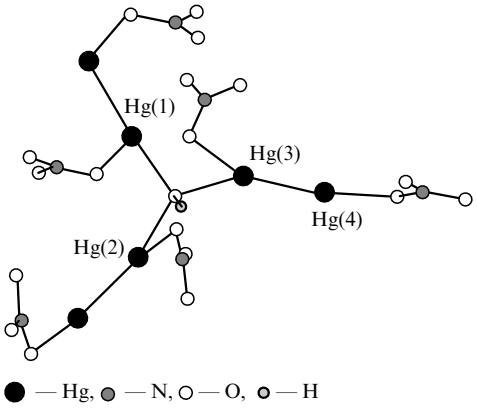


Figure 6. Fragment of the structure of $Hg_2OH(NO_3)\cdot Hg_2(NO_3)_2$.

The mercury pairs, which are linked in infinite $-O-Hg-Hg-O-Hg-Hg-O-$ chains *via* the XO_4^{2-} groups (X = S or Se), were observed in the isostructural Hg_2SO_4 and Hg_2SeO_4 compounds.[24] The chains intersect the unit cells along the diagonals nearly parallel to the *ac* planes. In Hg_2XO_4, there are Hg···O contacts (2.49 and 2.50 Å in Hg_2SO_4 and Hg_2SeO_4, respectively), which link chains. The $-O-Hg-Hg-O-$ fragments deviate from linearity (the Hg—Hg—O angles are 165° and 160° in Hg_2SO_4 and Hg_2SeO_4, respectively). No noticeable changes in the size and no distortions of the XO_4^{2-} tetrahedra are observed in the structures.

More than 30 compounds were found and described in the ternary $Hg_2O-N_2O_5-H_2O$ system.[25] In the studies devoted to the hydrolysis products of nitrate $Hg_2(NO_3)_2\cdot 2H_2O$,[26] the authors confirmed the existence of only three low-valent mercury oxonitrates, *viz.*, $[(Hg_2)_2O(NO_3)]NO_3\cdot HNO_3$ and $[(Hg_2)_5(OH)(NO_3)_2](NO_3)_2$ containing monovalent mercury and the mixed-valence $[(Hg)_2(OHg)_2](NO_3)_2$ compound.

In spite of the difficulties associated with the preparation of single crystals of these compounds, their structures were studied by X-ray diffraction analysis.[27] In the structure of $[(Hg_2)_2O(NO_3)]NO_3\cdot HNO_3$, three $(Hg_2)^{2+}$ pairs are linked together through the oxygen atoms (the Hg—O distances are 2.12, 2.19 and 2.31 Å) to form a planar (the height is 0.31 Å) trigonal pyramid with the O—Hg—O angles varying from 112.9 to 123.5°. The analogous function of the oxygen atom was pointed out in the structures of mercury(II) oxochloride Hg_3OCl_4 (see Ref. 28), the mineral eglestonite $(Hg_2)_3Cl_3O_2H$ (see Ref. 3) and in a number of other mercury compounds. The structure of $[(Hg_2)_2O(NO_3)]NO_3\cdot HNO_3$ as a whole consists of infinite mercury-oxygen chains linked in a three-dimensional framework through the NO_3^- ions, which coordinate the mercury atoms (the Hg···O contacts are in the range of 2.45–2.96 Å). The hydrogen atom was not located in the structure refinement of this compound. Based on the known data on the structures of the oxonium mercury salts, the authors[27] suggested that HNO_3 exists as a molecule of solvation linked to the nitrate ion through a hydrogen bond (O—H···O, 2.81 Å). The structure of this compound was more accurately established by an independent research group.[29] The position of the hydrogen atom of the hydroxy group was revealed. This group is coordinated to three $(Hg_2)^{2+}$ pairs (O—H, 1.26 Å) (Fig. 6). As a result, the structure is additionally stabilised through weak hydrogen bonds between the oxygen atoms of the hydroxy groups and the adjacent nitrate ions (Hg···O, 2.803–2.863 Å). Based on this fact, the authors[29] proposed that the formula of the compound should be written as $Hg_2OH(NO_3)\cdot Hg_2(NO_3)_2$.

The structure of the $[(Hg_2)_5(OH)(NO_3)_2](NO_3)_4$ compound contains the finite cationic $[(Hg_2)_5(OH)(NO_3)_2]^{4+}$ chains linked *via* weak van der Waals interactions between the adjacent mercury and oxygen atoms (Hg···O, 2.642 and 2.745 Å).[27,30] The chains form ribbons extended along the [100] direction. The $-O-Hg-Hg-O-$ fragments are virtually linear. The coordination environment about the mercury atoms involves the additional NO_3^- anions (Hg···O, 2.763–2.887 Å), which are responsible for the formation of a loose framework.

The structure of mercurous nitrophosphate $Hg_4PO_4NO_3\cdot \cdot H_2O$ is built of the PO_4^{3-} and NO_3^- anions and the water molecules bound to the $(Hg_2)^{2+}$ pairs, which form zigzag chains (the Hg—Hg distances are 2.508 and 2.532 Å; the Hg—O distances range from 2.11 to 2.21 Å; the Hg—Hg—O angles vary from 147 to 168°). These chains are linked in a three-dimensional framework through additional bonds.[31] No significant changes in the size and configuration of the anions in the crystal were observed.

The isostructural monophosphates and monoarsenates of silver and monovalent mercury were prepared as early as 1909. However, the crystal structure of $AgHg_2PO_4$ was established only in 1978.[32] The structure of the latter compound consists of the tetrahedral PO_4^{3-} anions and the Ag—Ag (2.824 Å) and Hg—Hg pairs (2.608 Å). Interestingly, this structure does not contain the linear $-O-M-M-O-$ fragments (M = Ag or Hg) typical of the above-considered compounds and each mercury atom is coordinated by three oxygen atoms of different PO_4 tetrahedra with elongated Hg—O bonds (2.224–2.346 Å). Therefore, the coordination environment about the mercury atoms in the Hg—Hg dimer is a tetrahedron (Hg + 3O). Each silver atom is coordinated by two oxygen atoms (Ag—O, 2.289 Å). The Hg—Hg and Ag—Ag dimers are in the mutually perpendicular arrangement and are rather closely spaced (the Hg—Ag distances are 2.840 and 2.941 Å). These data suggest the existence of the tetrahedral Ag_2Hg_2 clusters.

The three-dimensional $(Hg_4O^{2+})_n$ framework of hexagons formed by the $-O-Hg-Hg-O-$ fragments (Hg—Hg, 2.458 Å; Hg—O, 2.108 Å) was found in the crystal of the $Hg_4OPb_2(NO_3)_6$ compound.[33] The Pb^{2+} ions occupy the cavities of the framework and six statistically disordered NO_3^- groups act as bidentate ligands with respect to Pb^{2+} (Pb—O, 2.77–2.89 Å). The $Hg_4OBa_2(NO_3)_6$ compound isomorphous to $Hg_4OPb_2(NO_3)_6$ was also obtained.

Heteropolytungstate $K_5Cs_5[(Hg_2)_2WO(H_2O)(AsW_9O_{53})_2]$ was synthesised and structurally characterised for the first time in the study.[34] In this complicated structure, both $[As_2W_{19}Hg_4O_{67}(H_2O)]_{10}^-$ polyanions of one asymmetrical unit contain two $(Hg_2)^{2+}$ pairs, in which each mercury atom is bound to two oxygen atoms (the Hg—O distances vary from 2.16 to 2.34 Å). All eight mercury atoms of the asymmetrical unit form a distorted cube, whose vertices alternately correspond to the

covalent Hg—Hg bonds (2.446–2.545 Å) and the Hg···Hg distances (3.303–3.796 Å).

The structures of a series of mercury minerals containing the $(Hg_2)^{2+}$ pairs were analysed in detail.[2] These structures are also characterised by three-dimensional frameworks. Thus, in shakhovite $Hg_4SbO_3(OH)_3$, the O···O contacts (2.618–2.932 Å) between the oxygen atoms of the adjacent SbO_6 octahedra link these octahedra in layers parallel to the (001) plane, which, in turn, are linked in a three-dimensional framework through the $(Hg_2)^{2+}$ pairs (Fig. 7).[35]

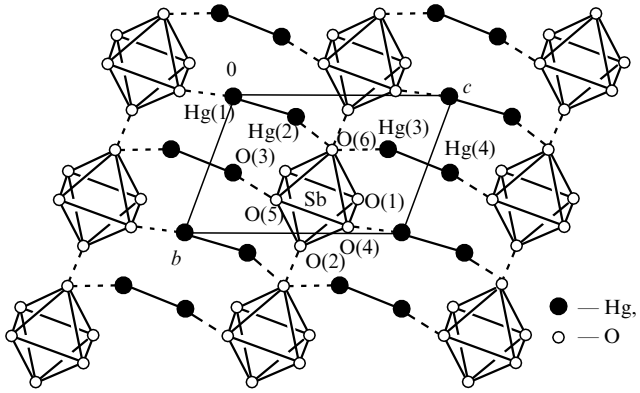


Figure 7. Projection of the crystal structure of shakhovite $Hg_4SbO_3(OH)_3$ onto the (100) plane. The O···O and Hg···O contacts are indicated by dashed lines.

In the crystal structure of the rare mineral poyarkovite Hg_3OCl, six $(Hg_2)^{2+}$ pairs were found;[36] the distances between the mercury atoms vary from 2.503 to 2.565 Å. The $(Hg_2)^{2+}$ cations are located along three mutually perpendicular directions. Each oxygen atom forms four tetrahedrally directed Hg—O bonds (1.94–2.51 Å) through which the mercury pairs are linked in a framework (Fig. 8).

The above-mentioned structure of the mineral eglestonite $(Hg_2)_3Cl_3O_2H$ (see Ref. 37) consists of four interpenetrating cubic three-dimensional frameworks $(Hg_2)_3O_2$ (see Ref. 1), in which the oxygen atoms are involved in three Hg—O bonds and link the $(Hg_2)^{2+}$ pairs located along each bond of the framework.

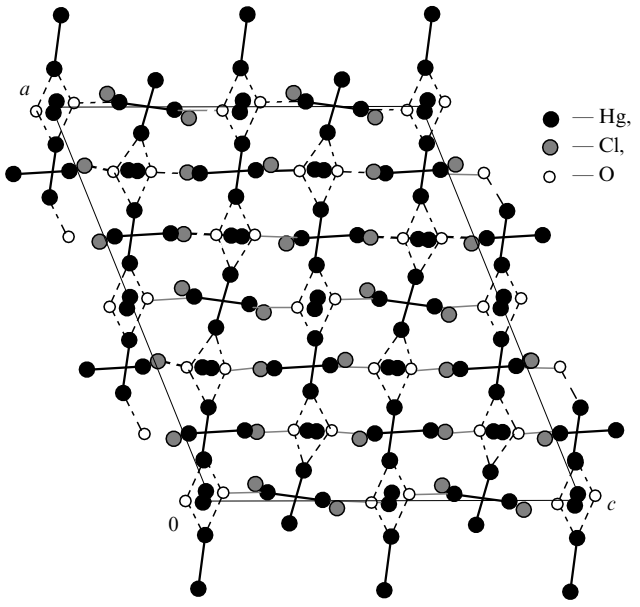


Figure 8. Systems of the mutually perpendicular $(Hg_2)^{2+}$ pairs in the structure of poyarkovite Hg_3OCl.

The frameworks are linked to each other through short O—H···O hydrogen bonds (O···O, 2.59 Å) and chlorine atoms.

In the structure of magnolite Hg_2TeO_3, the —O—Hg—Hg—O— fragments are linked *via* the tellurium atoms (Te—O, 1.93 Å) in zigzag chains extended along the [010] direction. The chains are linked through Hg···O contacts (2.692–2.998 Å). There are also short O···O distances (2.817 and 2.750 Å).[38]

The study of edgarbaileyite $Hg_6Si_2O_7$ demonstrated [39] that the Hg—Hg pairs in this structure are parallel to each other and the —O—Hg—Hg—O— fragments are virtually linear. Each mercury atom is additionally coordinated by two oxygen atoms (the Hg—O distances are 2.41–2.86 Å). The Si_2O_7 groups are located between the mercury pairs and are linked in a framework through the Hg—O bonds (2.21 and 2.63 Å).

The distinguishing feature of the structure of szymanskiite $Hg_{16}(Ni,Mg)_6(CO_3)_{12}(OH)_{12}(H_3O)_8 \cdot 3H_2O$ is that the MO_6 octahedra (M = Ni or Mg) are linked to the linear —O—Hg—Hg—O— fragments in a rigid framework with large channels (the diameter is 13.6 Å) (Fig. 9).[40] The channels are occupied by the disordered CO_3 groups and the water molecules, which are rather weakly bound to each other. This gives grounds to consider this mineral as a nonsilicate zeolite. Note that in the structure of szymanskiite, like in the structure of $AgHg_2PO_4$ (see Ref. 32), the mercury atoms belonging to one type of the $(Hg_2)^{2+}$ pairs have an umbrella-shaped coordination with the involvement of three oxygen atoms of the CO_3 groups located at longer distances (Hg—O, 2.34 and 2.44 Å). This coordination is rarely observed in monovalent mercury compounds.

Analysis of the structures of inorganic compounds containing $(Hg_2)^{2+}$ groups with different ligands demonstrates that the Hg—Hg distances vary from 2.45 to 2.59 Å. No distinct correlations between the Hg—Hg and Hg—X distances in the X—Hg—Hg—X groups and the nature of inorganic ligands X were observed. In the series of the compounds with the NO_3^-, BrO_3^-, TeO_3^{2-} and VO_3^- ligands, the Hg—Hg distances increase from 2.50 to 2.54 Å, which can be related to a decrease in the electronegativity of the ligands in this series of anions. In the series of the compounds with the ReO_4^-, PO_4^{3-} and AsO_4^{3-} ligands, the Hg—Hg distances vary from 2.506 to 2.535 Å. The shortest distance was observed in the $HgReO_4$ compound because the total negative charge of the ReO_4^- anion is smaller than the effective negative charge of the oxygen atom due to the higher oxidation state of the rhenium atom compared to the phosphorus and arsenic atoms. The increase in the Hg—Hg distance from 2.50 Å in mercury nitrate to 2.52 Å in mercury nitrite can also be attributed to the lower degree of oxidation of the nitrogen atom in the NO_2^- anion compared to that in the NO_3^- anion. The longest Hg—Hg distance in the three-dimensional Hg—O framework (2.56 Å) is observed if the coordinating oxygen atoms bind only

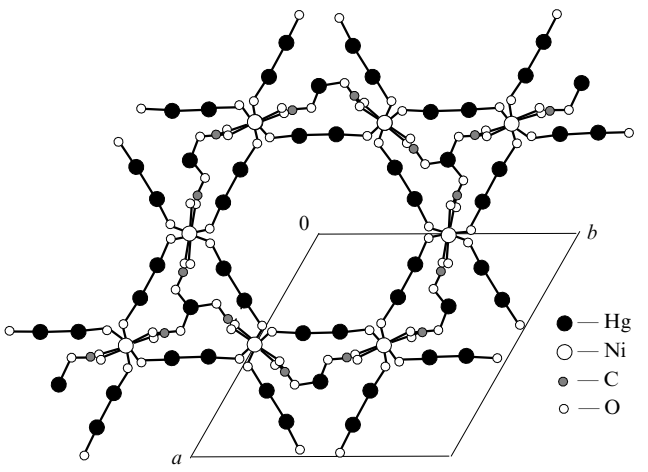


Figure 9. Fragment of the crystal structure of szymanskiite.

$(Hg_2)^{2+}$ groups, *i.e.*, a competing cation is absent. An increase in the Hg—Hg distance can also occur, apparently, due to an increase in the covalence of the Hg—X bond.[5]

A noticeable effect of a strong metal—metal bond on the configuration of compact tetrahedral SO_4^{2-}, SiO_4^{4-}, PO_4^{3-} and AsO_4^{3-} anions was observed only in some instances, for example, in the $(Hg_2)_3(AsO_4)_2$ compound.[23] An increase in the length of one Br—O bond compared to the remaining bond lengths was also found in $Hg_2(BrO_3)_2$.[14]

Hence, the coordination of the mercury atoms in oxygen-containing compounds is generally linear with one short Hg—O distance (~2.10 Å) and one-to-two additional atoms located at substantially larger distances. In the mineral szymanskiite and in phosphate $AgHg_2PO_4$, some mercury atoms in the Hg—Hg dimers are nonlinearly coordinated by the oxygen atoms [an umbrella of three oxygen atoms with the larger Hg—O distances (2.22–2.44 Å)].

III. Mixed-valence inorganic mercury compounds

The data on a number of rather rare mixed-valence compounds containing Hg^{2+} cations and Hg_n groups ($n = 2$ or 3), in which the oxidation state of the mercury atoms is lower than +2, are available. The principal crystal-structural characteristics of these compounds are given in Table 1.

The existence of a compound containing mercury in two oxidation states, *viz.*, in +2 and +1, was first reported in a study,[41] in which the results of X-ray diffraction study of the synthetic analogue of the rare mineral terlinguaite $Hg_4O_2Cl_2$ were discussed. Several studies were devoted to the crystal structures of the natural samples and their synthetic analogues.[41–44] The studies confirmed the fact that the mercury atoms in terlinguaite exist in different oxidation states, *viz.*, in +2 and +4/3 (in the unique triangular Hg_3 clusters).

Two new mercury oxohalides, *viz.*, the bromine and iodine analogues of terlinguaite, were synthesised in the study.[45] Dark-red platelet-like crystals of Hg_2OI were grown by the hydrothermal method at 450 K from a stoichiometric mixture of HgO and Hg_2I_2. X-Ray diffraction study of the resulting compound, whose stoichiometry is identical to that of terlinguaite, demonstrated that this compound, though also mixed-valence, has quite a different structure. The structure of Hg_2OI (see Ref. 46) consists of infinite zigzag chain $Hg^{2+}—O—Hg^{2+}$ along the *b* axis. These chains are linked through the $(Hg_2)^{2+}$ pairs to form 14-membered rings, which, in turn, are linked in a three-dimensional framework through weak additional $Hg^{2+}\cdots O$ bonds (2.47 Å) (Fig. 10). The iodine atoms occupy the cavities in the layers and form weak contacts with the Hg^{2+} cations. The coordination $Hg^{2+}—O$ bonds in the structure of Hg_2OI are somewhat longer (2.13 and 2.16 Å) and the $O—Hg^{2+}—O$ angles are smaller (165°) than the corresponding values in divalent mercury compounds.[47] Apparently, this is attributable to the contacts of the Hg^{2+} cation with the oxygen atom (2.47 Å) and with the iodine atoms (3.05 and 3.14 Å). Taking into account these weak bonds, the coordination polyhedron about Hg^{2+} can be described as a distorted square pyramid. The mercury atoms of the $(Hg_2)^{2+}$ pairs are linearly coordinated by the oxygen atoms and the shortest $(Hg_2)^{2+}\cdots I$ distance is 3.47 Å.

In the middle 80s, two research groups[27,48] independently prepared and studied lemon-yellow crystals of the hydrolysis product of $Hg_2(NO_3)_2\cdot 2H_2O$, *viz.*, the mixed-valence $Hg_4O_2(NO_3)_2$ compound, whose stoichiometry is identical to that of Hg_2OI. These compounds are partially similar in structure. In the crystal structure of $Hg_4O_2(NO_3)_2$, as in the structure of Hg_2OI, the $O—Hg^{2+}—O$ chains and the $(Hg_2)^{2+}$ pairs also form analogous 14-membered rings. However, unlike the structure of Hg_2OI, the rings in $Hg_4O_2(NO_3)_2$ are linked in corrugated layers parallel to the (201) plane (Fig. 11) rather than in a three-dimensional framework. The Hg—Hg (2.510 Å) and Hg—O (2.136 Å) bonds within the layers are covalent and the layers are

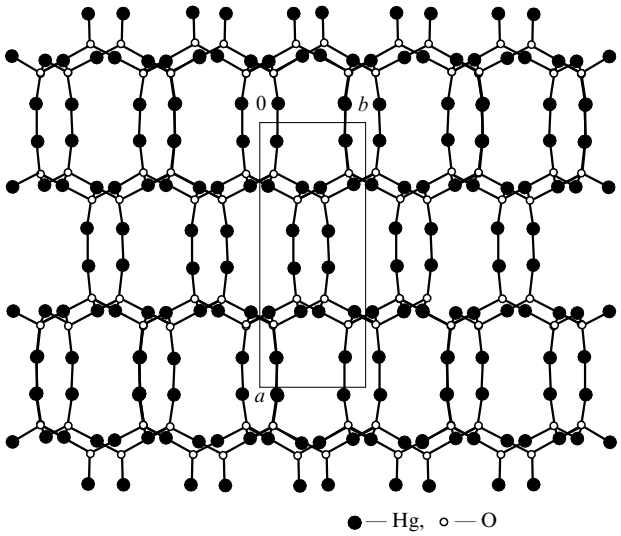


Figure 10. Framework of the 14-membered $[-(Hg_2)_2^{2+}—O_6—Hg_4^{2+}—]$ rings in the structure of Hg_2OI.

linked through the weak $(Hg_2)^{2+}\cdots O$ contacts (2.84 Å) and the NO_3^- ions, which act as bridging ligands for the mercury atoms. This layered structure accounts for the noticeable cleavage of the crystals of $Hg_4O_2(NO_3)_2$ parallel to the (201) plane. The coordination numbers of the Hg^{2+} cation and the mercury ions in the $(Hg_2)^{2+}$ pair are equal to 2. It is worthy of note that the bonds between the mercury atoms of the $(Hg_2)^{2+}$ pair and the oxygen atoms are substantially longer than the $Hg^{2+}—O$ distances.

In attempting to synthesise the bromine analogue of terlinguaite, *viz.*, Hg_2OBr (see Ref. 45) (hydrothermal synthesis at 460 K from a stoichiometric mixture of HgO and Hg_2Br_2), crystals with composition $Hg_8O_4Br_3$, were obtained and studied by X-ray diffraction analysis.[49] The structure of $Hg_8O_4Br_3$ differs from the structures of terlinguaite $Hg_4O_2Cl_2$,[44] Hg_2OI[46] and $Hg_4O_2(NO_3)_2$.[27,48] There are five independent routes by which monovalent mercury atoms form three $(Hg_2)^{2+}$ pairs (2.517–2.557 Å) and three independent Hg^{2+} ions per asymmetric unit. The metal atoms in the $(Hg_2)^{2+}$ pairs have the oxygen

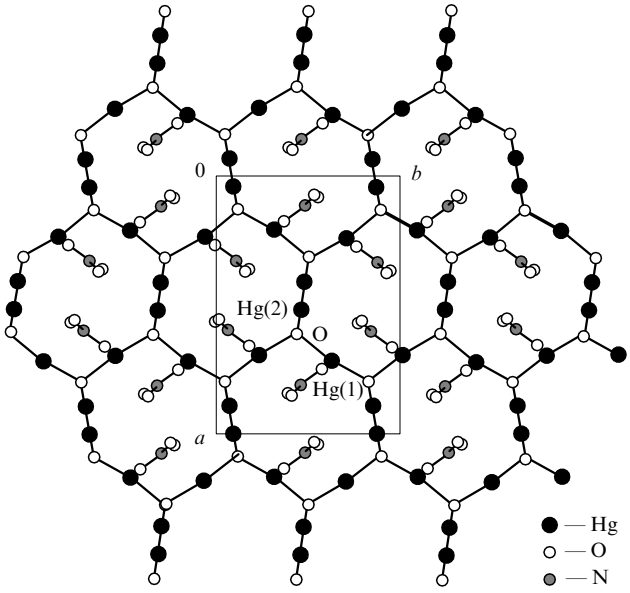


Figure 11. Layer of the 14-membered $[-(Hg_2)_2^{2+}—O_6—Hg_4^{2+}—]$ rings in the structure of $Hg_4O_2(NO_3)_2$.

atoms as the nearest neighbours at distances of 2.14–2.24 Å through which the 12-membered $[-O-(Hg_2)^{2+}-]_4$ rings are formed. These rings are linked in infinite chains *via* the $(Hg_2)^{2+}$ dimers (Fig. 12). The Hg^{2+} ions coordinated by the oxygen atoms form helical chains (the $Hg^{2+}-O$ distances vary from 2.01 to 2.18 Å) similar to those found in two modifications of HgO.[50, 51] The oxygen atoms bind the 'divalent' and 'monovalent' portions of the structure to form a three-dimensional framework with the bromine atoms located in the cavities (the shortest Hg···Br contact is 3.02 Å).

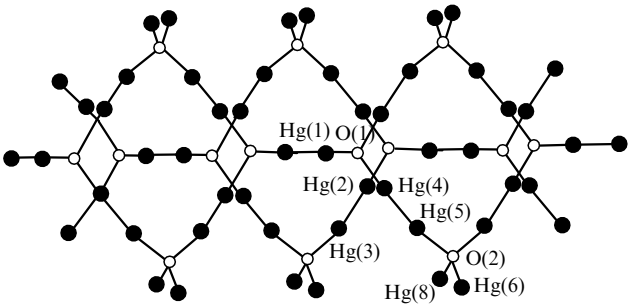


Figure 12. 12-Membered $[-O-(Hg_2)^{2+}-O-]$ rings linked through the $(Hg_2)^{2+}$ pairs in the structure of $Hg_8O_4Br_3$.

In the ternary Hg–Re–O system, four compounds containing formally monovalent mercury,[15] *viz*., $HgReO_4$, and mixed-valence $Hg_5Re_2O_{10}$ (two modifications) and Hg_2ReO_5, were structurally characterised. Unlike the molecular structure of $HgReO_4$, all three mixed-valence compounds have polymeric structures. The polycations of the fused $[(Hg_2)^{2+}-O-(Hg^{2+})-O]_n$ rings of different types form puckered two-dimensional infinite networks separated by the tetrahedral ReO_4^- anions.

The structure of Hg_2ReO_5 (see Ref. 15) contains 14-membered rings consisting of the oxygen atoms, Hg^{2+} cations and $(Hg_2)^{2+}$ pairs, which are analogous to those found in the structure of $Hg_4O_2(NO_3)_2$ (see Refs 27 and 48). These rings are linked in infinite two-dimensional (but with another type of corrugation) polycationic $[(Hg_2)^{2+}\cdot 2HgO]_n$ networks.

A comparison of two modifications of $Hg_5Re_2O_{10}$ suggested that these compounds have related structures.[52, 53] Both compounds contain two-dimensional infinite corrugated networks with composition $[Hg^{2+}\cdot 2(Hg_2)^{2+}O]_n$, which are separated by the tetrahedral ReO_4^- cations. The networks in the first modification of $Hg_5Re_2O_{10}$ consist of fused 16-membered rings.[52] The networks in the second modification contain the 10- and 22-membered rings [53] (Fig. 13). Analogous networks were also found in the structure of Hg_3CrO_6.[54]

Presently, the structures of about ten mercury oxovanadates are known, among which are two compounds containing mercury in the formal oxidation state of +1, *viz*., $HgVO_3$ and the mixed-valence Hg_2VO_4 compound.[19] The architecture of the crystal structure of Hg_2VO_4 is very unusual, namely, the $(Hg_2)^{2+}$ pairs and the Hg^{2+} ions together with certain of the oxygen atoms form infinite helical chains, which are located on the surface of the adjacent infinite channels in such a manner that the structure projected along the short *a* period appears as the structure consisting of fused 14-membered rings similar to those described above in the structures of Hg_2OI,[46] $Hg_4O_2(NO_3)_2$ [27, 48] and Hg_2ReO_5.[15] The mercury ions in the $(Hg_2)^{2+}$ pairs and the Hg^{2+} cations have a normal linear coordination. The trigonal-bipyramidal VO_5 groups are linked *via* shared edges to form infinite $[(VO_3)^-]_n$ chains parallel to each other and located in the centres of mercury–oxygen channels. These chains have no strong bonds with mercury atoms (Hg···O > 2.57 Å). The formula of this compound can be described as follows: $[(Hg_2)^{2+}\cdot 2(Hg^{2+}O)]_n\cdot[(VO_3)^-]_{2n}$.

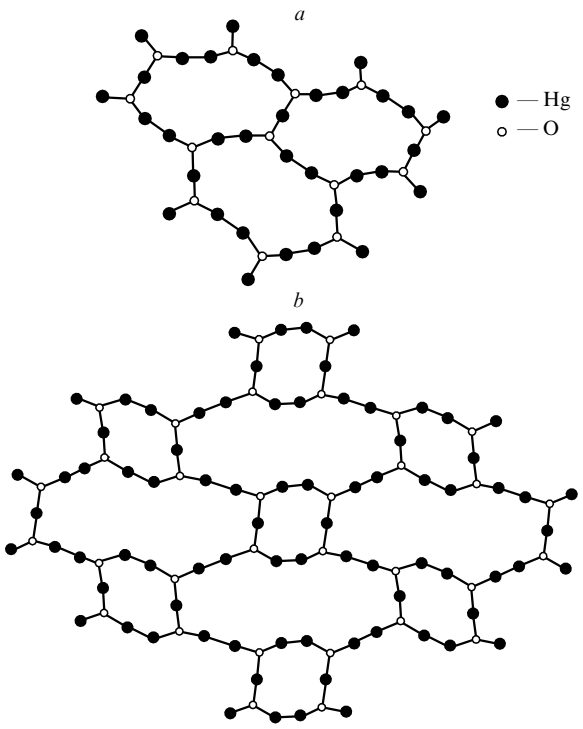


Figure 13. Types of the Hg–O rings in the crystal structures of two modifications of $Hg_5Re_2O_{10}$. Modification: (*a*) I; and (*b*) II.

The new $Hg_9P_5I_6$ compound,[55] which possesses semiconducting properties, contains the mercury and phosphorus atoms in different oxidation states (+2, +1 and −3, −2, respectively), the low-valent phosphorus atoms existing as $(P_2)^{2-}$ dimers with the P–P distance of 2.10 Å. The Hg^{2+} ions form tetrahedra about the phosphorus atoms and octahedra, whose centres are occupied by the $(P_2)^{2-}$ dimers. The P_2Hg_6 octahedra are linked *via* shared vertices to form layers parallel to the (100) plane. These layers are linked through the ditetrahedral P_2Hg_7 groups and the $(Hg_2)^{2+}$ pairs. In this structure, the P–Hg–P and P–Hg–Hg groups have an almost linear configuration. The coordination environment about the mercury atoms is completed by the iodine atoms (the Hg–I distances vary from 3.097 to 3.691 Å). Taking into account the different valence states of the mercury and phosphorus atoms, it was suggested [55] that the formula of the compound be written as $(Hg-Hg)^{2+}Hg_{16}^{2+}(P-P)_4^{4-}P_2^{3-}I_{12}$.

Presently, only a few natural mixed-valence mercury compounds are known. These compounds, like the rare minerals containing only $(Hg_2)^{2+}$ pairs, are very unstable. The X-ray structural studies of these compounds are very laborious. Recently, the crystal structures of three natural mercury chromates, *viz*., edoylerite $(Hg^{2+})_3S_2CrO_4$ (Ref. 56), deanesmithite $(Hg^+)_2(Hg^{2+})_3OS_2CrO_4$ (Ref. 57) and wattersite $(Hg^+)_4Hg^{2+}O_2CrO_4$ (Ref. 58), have been studied. The last two mixed-valence compounds represent new structural types containing the polymeric $-O-Hg-O-$ and $-O-(Hg_2)^{2+}-O-$ fragments typical of mercury compounds. In the structure of sulfur-containing deanesmithite, the infinite $\cdots(Hg_2)^{2+}-O-Hg^{2+}-O-(Hg_2)^{2+}-[(Hg^{2+}-S)_6]-(Hg_2)^{2+}\cdots$ chains involving the 12-membered $[(Hg_2)^{2+}-S]_6$ rings can be distinguished. The $O-(Hg_2)^{2+}-S$ groups are virtually linear.

In wattersite $(Hg^+)_4Hg^{2+}O_2CrO_4$, the CrO_4 tetrahedra and the distorted Hg^{2+} octahedra form ribbons with composition $[Hg^{2+}CrO_6]^{6-}$, which are linked in slightly distorted layers parallel to the (100) plane through the $(Hg_2)^{2+}$ pairs.

In the structure of natural mercury oxochloride, *viz*., in the mineral hanawaltite $(Hg^+)_6Hg^{2+}O_3Cl_2$, the $-O-Hg^{2+}-O-$ and $-O-(Hg_2)^{2+}-O-$ fragments form a three-dimensional framework whose cavities are occupied by the chlorine atoms.[59]

The distinguishing feature of this structure is that all $(Hg_2)^{2+}$ pairs lie approximately in the (001) plane and form corrugated layers. The researchers attributed the planar (001) habit of the mineral to the presence of strong Hg–Hg bonds in this plane and ascribed the good cleavage in the direction perpendicular to the *c* axis to weak bonds, which occur between the layers along this direction through the Hg^{2+} ions.

Another natural mercury oxochloride, *viz*., the above-mentioned terlinguaite $Hg_4O_2Cl_2$,[44] contains alternating layers of $\{Hg^{2+}Cl_2\}$ and $\{(Hg_3)^{4+}O_2\}$. The latter layers contain the triangular $(Hg_3)^{4+}$ clusters (Hg–Hg, 2.707 Å), which are in a single plane (Fig. 14). The resulting structure may be represented as a three-dimensional mercury-oxygen framework with Cl atoms in the cavities. The layers containing strong Hg–Hg bonds are responsible for the anisotropy of the physical properties of hanawaltite and terlinguaite.

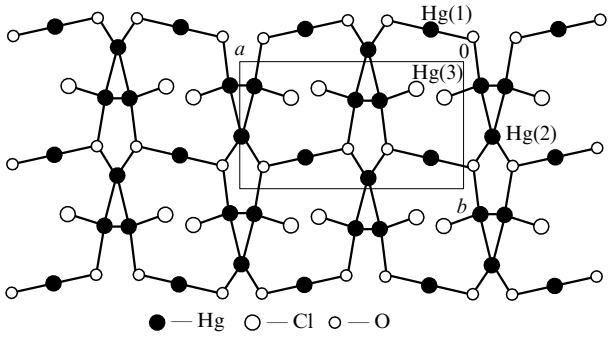


Figure 14. Crystal structure of terlinguaite $Hg(Hg_3)O_2Cl_2$.

Only three inorganic mercury compounds, whose structures contain the triangles $(Hg_3)^{4+}$ in which the mercury atoms exist in the formal oxidation state of +4/3, are known. Hence, although two compounds considered below are not mixed-valence, it is reasonable to describe their structures in this section. Recently, the crystal structure of the rare hypergene mineral kuznetsovite Hg_3AsO_4Cl, whose structure has been previously established based on X-ray powder data,[61] was refined.[60] This is the second naturally occurring compound containing the cyclic $(Hg_3)^{4+}$ group (Hg–Hg, 2.675 Å). In the cubic structure, the Hg_3 triangles and the AsO_4^{3-} tetrahedra alternate along all crystallographic axes (Fig. 15). Taking into account only short Hg–O bonds (2.17 and 2.28 Å), a framework can be distinguished. The cavities of this framework are occupied by the chlorine atoms in a diamond-like fashion.

The third compound, *viz*., pale-yellow crystals of $Hg_9As_4O_{16}$, was prepared upon thermal decomposition (550 °C) of $(Hg_2)_3(AsO_4)_2$.[62] The crystal structure of this compound consists of the $(Hg_3)^{4+}$ triangles (Hg–Hg, 2.662–2.696 Å) and the AsO_4^{3-}

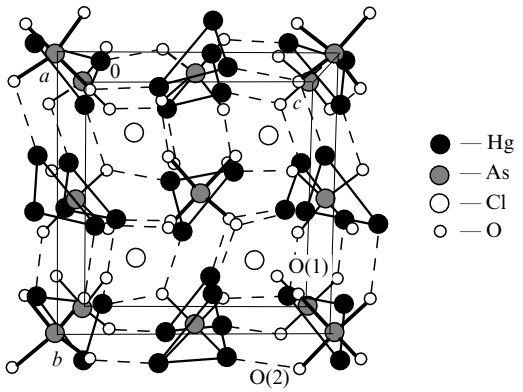


Figure 15. Crystal structure of kuznetsovite Hg_3AsO_4Cl.

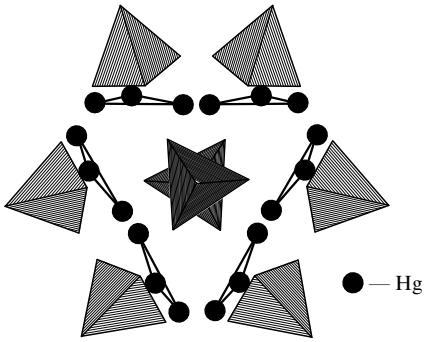


Figure 16. Arrangement of the Hg_3 triangles and the AsO_4 tetrahedra in the crystal structure of $(Hg_3)_3(AsO_4)_4$.

tetrahedra and corresponds to the formula $[(Hg_3)^{4+}]_3[(AsO_4)^{3-}]_4$. The coordination environment about the mercury atoms is a distorted tetrahedron with the Hg–O distances of 2.14–2.34 Å. The remaining distances vary from 2.58 to 2.93 Å (Fig. 16).

The tendency of mercury-oxygen groups to polymerisation, which is characteristic of divalent mercury compounds, is retained in compounds containing mercury atoms in different oxidation states.[47] The pairs of the monovalent mercury atoms form the linear $O-(Hg_2)^{2+}-O$ groups, which (along with the linear $O-Hg^{2+}-O$ units) are involved in the formation of polycations of different types, *viz*., rings, infinite chains, corrugated and planar networks, layers or frameworks. The triangular $(Hg_3)^{4+}$ group plays a similar role. Fragments containing the groups of monovalent mercury are characterised by larger deviations from linearity (the Hg–Hg–O angles are 145–178 °) and by elongated Hg–O bonds (2.10–2.34 Å) compared to the groups containing Hg^{2+} (the O–Hg–O angle is 180 °; the average Hg–O distance is 2.06 Å). Apparently, this is due to the effect of the strong metallic Hg–Hg bond, whose length changes only slightly and is virtually independent of the coordination environment about the mercury atoms.

Analysis of the bond lengths in the mixed-valence and cluster mercury derivatives demonstrates that the divalent mercury atoms are not only linearly coordinated by two atoms with the shortest distances, but also are generally surrounded by several atoms located at distances of > 2.5 Å. When describing the structures, these atoms are often included in the coordination environment about the mercury atoms. Since the environment about the mercury atoms is often formed by atoms of different types, the spread in the distances in the polyhedra is large and the polyhedra are strongly distorted. This is also true for the environment about the monovalent mercury atoms in the $(Hg_2)^{2+}$ pairs and $(Hg_3)^{4+}$ triangles. The description of the coordination polyhedra about the individual mercury atoms becomes even more arbitrary in the presence of strong metallic bonds because these polyhedra are very distorted.

From the crystal-chemical standpoint, it is worthwhile to consider this series of structures as structures containing the overall complex Hg_n^{x+} cations with the coordinates of the geometric centres of the complexes and to describe the coordination environment about the Hg_n^{x+} cation as a whole. For example, the environment about the $(Hg_2)^{2+}$ pair in the structure of chursinite $(Hg_2)_3(AsO_4)_2$ is a trigonal antiprism formed by the oxygen atoms of the AsO_4 tetrahedra [23] (Fig. 17 *a*). In the study of the structure of kuznetsovite Hg_3AsO_4Cl, [61] the environment about the triangular mercury cluster was described as a convex 16-vertex polyhedron, *viz*., Friauf's polyhedron (Fig. 17 *b*) formed by twelve oxygen atoms and four chlorine atoms. The application of this approach to other structures demonstrated that the environment about the $[Hg_3]^{4+}$ cation (6O + 6Cl) in terlinguaite $Hg(Hg_3)O_2Cl_2$ is a hexagonal analogue of cuboctahedron (Fig. 17 *c*)[44] and the environment about the analogous cation in $(Hg_3)_3(AsO_4)_4$ is a cuboctahedron formed by 12 oxygen atoms

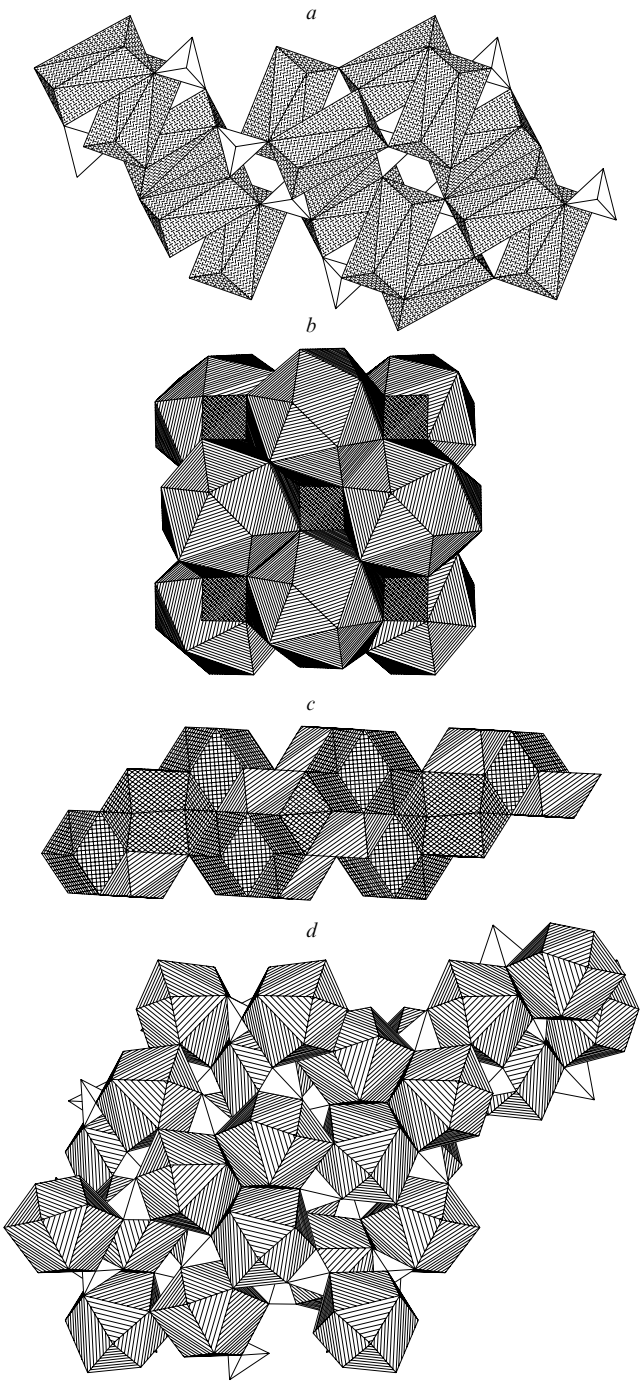


Figure 17. Coordination Hg_n polyhedra in the structures of $(Hg_3)_2.(AsO_4)_2$ (*a*), Hg_3AsO_4Cl (*b*), $Hg(Hg_3)O_2Cl_2$ (*c*) and $(Hg_2)_3(AsO_4)_4$ (*d*).

(Fig. 17 *d*).[62] The symmetry and the convexity of the coordination polyhedron as well as a small spread in the distances from the centre of the mercury group to the vertices of the polyhedra and a small spread in the lenghts of the edges of the polyhedron can serve as criteria for choosing the polyhedral environment about the Hg_n^{x+} cation. Note that this method would never do for describing the coordination environment about cluster mercury groups if the distances between the atoms of the adjacent mercury groups are close to the cation–anion bond lengths [for example, in the structure of poyarkovite Hg_3OCl,[36] in which the shortened distances (3.11–3.13 Å) were observed between the mercury atoms of some adjacent $(Hg_2)^{2+}$ pairs].

IV. Compounds containing polyatomic Hg_n^{x+} cations ($n > 2$)

Salts, which contain linear Hg_n^{x+} systems of metal atoms directly bound to each other (where $n > 2$, *i.e.*, the formal oxidation state of mercury is lower than +1) as ions, are formed in strongly acidic nonaqueous solvents and exist as stable crystalline compounds with particular anions.[1] For example,[63] the reactions of mercury with AsF_5 and SbF_5 in liquid SO_2 yielded the $(Hg_3)^{2+}$ and $(Hg_4)^{2+}$ ions, which were isolated as crystalline salts with the AsF_6^- and $Sb_2F_{11}^-$ anions. Attempts to prepare analogous salts with other anions according to this procedure failed, apparently, due to the fact that no other pentafluorides, which can oxidise mercury in an SO_2 medium at room temperature, were found. More recently, a universal procedure was developed for the preparation of compounds with the $(Hg_3)^{2+}$ and $(Hg_4)^{2+}$ cations, which involves the reaction of mercury with hexafluorides $Hg(MF_6)_2$. Dull-yellow crystals of $Hg_3(AsF_6)_2$ and dark-red crystals of $Hg_4(AsF_6)_2$ as well as analogous compounds with niobium, tantalum and antimony were prepared according to this procedure.[64] The reaction of mercury and $HgCl_2$ in a melt of $AlCl_3$ afforded the $Hg_3(AlCl_4)_2$ compound.[65] It should be noted that all these salts undergo rapid disproportionation in the presence of water to form elemental mercury and $(Hg_2)^{2+}$ salts. The principal crystal-structural data for compounds of this type are given in Table 1.

X-Ray diffraction studies of the $Hg_3(AsF_6)_2$ (see Ref. 63) and $Hg_3(AlCl_4)_2$ (see Ref. 66) compounds revealed the linear groups of the mercury atoms of the $(Hg_3)^{2+}$ type. The Hg–Hg bond lengths in these groups have equal or close values. Thus, the structure of $Hg_3(AlCl_4)_2$ consists of discrete molecules with the linear central –Cl–Hg–Hg–Hg–Cl– skeleton (the Hg–Hg bond lengths are 2.551 Å and 2.562 Å), which involves the chlorine atoms of the tetrahedral $AlCl_4$ groups, whereas in the structure $Hg_3(AsF_6)_2$ containing the $(Hg_3)^{2+}$ cations and the octahedral AsF_6^- anions, the $(Hg_3)^{2+}$ cation is linear and centrosymmetrical with the Hg–Hg bond length of 2.552 Å (Fig. 18). The Hg···F contacts between the terminal mercury and fluorine atoms of the adjacent AsF_6^- anions (2.38 Å) are collinear with the Hg–Hg bonds. These contacts are, most likely, covalent in character because their lengths are intermediate between the reference values of 2.10 and 2.46 Å, respectively.[63]

The $Hg_3(NbF_5)_2SO_4$ and $Hg_3(TaF_5)_2SO_4$ compounds are isostructural and also contain the nearly linear centrosymmetrical $(Hg_3)^{2+}$ cations linked to the $[F_5MOSO_2OMF_5]^{2-}$ anions

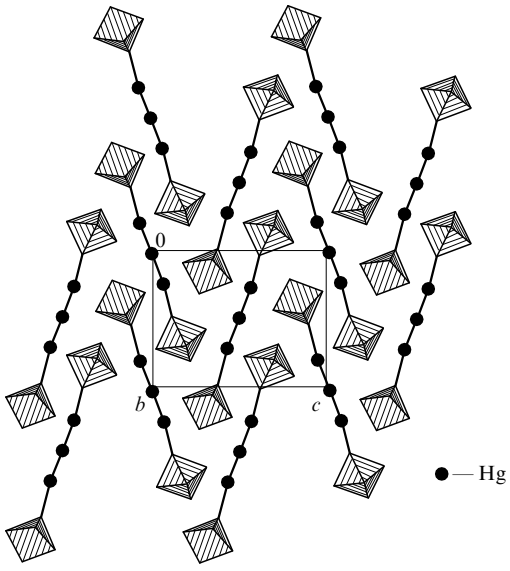


Figure 18. Linear $(Hg_3)^{2+}$ cations in the crystal structure of $Hg_3(AsF_6)_2$.

(M = Nb or Ta) through the terminal oxygen atoms to form chains along the [110] and [1$\bar{1}$0] directions.[67] The coordination environment about the mercury atoms in the $(Hg_3)^{2+}$ cations is analogous to those observed in $Hg_3(AsF_6)_2$ (see Ref. 63) and $Hg_3(AlCl_4)_2$ (see Ref. 66).

The structure of the $(Hg_4)^{2+}$ ion was established in the studies of the crystal structures of $Hg_4(Ta_2F_{11})_2$ (see Ref. 67) and $Hg_4(AsF_6)_2$ (see Ref. 68). The terminal Hg–Hg bonds (2.630 Å[67] and 2.620 Å[68]) in these compounds are somewhat longer than the central bonds (2.593 and 2.588 Å, respectively) and the bonds in the $(Hg_3)^{2+}$ cation.[63,66] The structures of these compounds consist of the nearly linear $(Hg_4)^{2+}$ cations (the Hg–Hg–Hg angles are 177.3 and 177.4°, respectively) and the $Ta_2F_{11}^-$ and AsF_6^- anions, respectively. The distinguishing feature of these structures is that the distances between the adjacent $(Hg_4)^{2+}$ cations (3.033 Å[67] and 2.985 Å[68]) are close to the shortest Hg–Hg distance in metallic mercury (2.99 Å).[69] Hence, taking into account these contacts, the $(Hg_4)^{2+}$ cations can be considered as being linked in infinite zigzag chains (along the *c* axis) with weak interactions between the terminal mercury atoms (Fig. 19). Thus, the interaction between the $(Hg_4)^{2+}$ cation and the AsF_6^- anion in the $Hg_4(AsF_6)_2$ compound in the direction nearly collinear with the terminal Hg–Hg bonds may be considered as being replaced by the Hg···Hg intercationic interaction at an angle of 124° to the terminal Hg–Hg bond [107.9° in $Hg_4(Ta_2F_{11})_2$] and by several weak Hg···F contacts with the anions. The latter contacts are substantially longer (> 2.7 Å) than the short interactions (2.38 Å) in $Hg_3(AsF_6)_2$, which are collinear with the Hg–Hg bonds, and are similar in length to the analogous contacts in other compounds with noncollinear Hg···F interactions (for example, the shortest Hg···F contacts in $Hg_{2.86}AsF_6$ are 2.87 and 2.98 Å).[70,71]

The reactions of mercury with AsF_5, SbF_5 or $Hg(MF_6)_2$ (M = Nb or Ta) on the surface of liquid mercury afforded gold-coloured crystals, which were similar in appearance to metallic crystals and existed for 10–15 min. Then these crystals were converted into soluble $(Hg_3)^{2+}$ salts. It was possible to store and isolate these crystals by choosing a weaker oxidising agent. These crystals appeared to be the most interesting substance among the compounds of the general formula $Hg_{3-\delta}MF_6$ (M = As, Sb, Nb or Ta) because they posses anisotropic metallic conductivity. The $Hg_{3-\delta}AsF_6$ and $Hg_{3-\delta}SbF_6$ compounds exhibit superconducting properties at low temperatures (T_c = 4 and 14 K, respectively).[64]

The crystal structure of the unique anisotropic superconductor of the empirical formula Hg_3AsF_6 can be described as a sublattice containing the octahedral AsF_6^- anions arranged in the tetragonal unit cell in a cubic close packing fashion.[70] There are linear nonintersecting channels in two nearly perpendicular directions (parallel to the *a* and *b* axes) within this sublattice. The infinite disordered chains of the mercury atoms in the formal oxidation state of +1/3 (Hg–Hg, 2.64 Å) are located along these channels (Fig. 20). The unit cell parameters $a = b = 7.54$ Å are not proportional to the threefold Hg–Hg distance (7.92 Å).

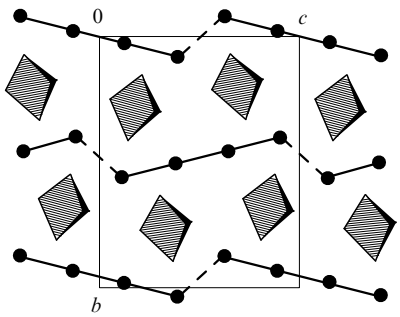


Figure 19. Linear $(Hg_4)^{2+}$ cations in the crystal structure of $Hg_4(AsF_6)_2$. The bonds between the cations are indicated by dashed lines.

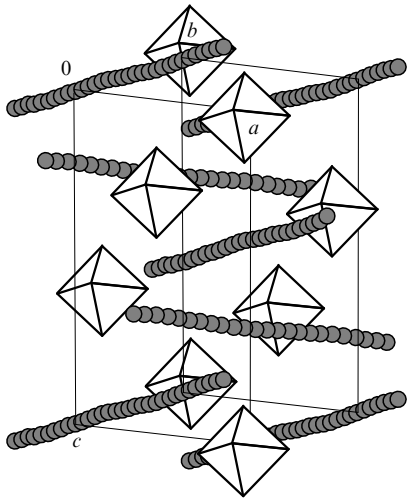


Figure 20. Infinite disordered Hg_n chains in the structure of $Hg_{3-\delta}AsF_6$.

Hence, the empirical formula of the compound under consideration can be formally obtained from the ratio 7.54 : 2.64 = 2.86 and may be written as $Hg_{2.86}AsF_6$.. Neutron diffraction study of Hg_3AsF_6 confirmed the formula $Hg_{2.86}AsF_6$ and the above-described crystal structure of the compound.[71]

However, according to the structural data, the disordered Hg_n chains are not precisely one-dimensional and the sites of the mercury atoms are only partially occupied. In addition, the maximum deviation of the mercury atoms from the axes of the chains in the [001] direction was 0.07 Å at room temperature and the shortest Hg–Hg contacts between the chains are 3.24 Å. If the chains were exactly linear, these distances would be $c/4$ = 3.098 Å. It was concluded [71] that the incommensurate structure is stabilised by anionic vacancies so that the unit cell contains four $Hg_{2.86}(AsF_6)_{0.953}$ formula units.

Hence, the structure of $Hg_{2.86}AsF_6$ contains the unique metal-bonded infinite polymeric cations, which form a portion of the ionic crystal lattice. The shortest contacts between the mercury and fluorine atoms (2.99 Å) are somewhat larger than the sum of the van der Waals radii (2.85 Å), *i.e.*, the crystal structure contains the AsF_6^- anions and the Hg_n chains, in which the average charge on the mercury atoms is equal to $1/2.86 = +0.35$. In this crystal, the ionic character of the bonds between the positively charged Hg_n chains and the AsF_6^- anions predominates. In addition, it should be noted that the Hg–Hg distance (2.64 Å) is substantially shorter than that in metallic mercury (2.99 Å). However, the coordination number of Hg in metallic mercury is 12, whereas in the compound under consideration, this value is equal to 2. The character of the structure under consideration is consistent with the anisotropy of conductivity in the crystal along the *a* and *b* axes.

The syntheses of a series of compounds with nonstoichiometric compositions of the general formula $Hg_{3-\delta}MF_6$ (M = Sb,[72] Nb or Ta [73]) at room temperature and of the general formula $Hg_{3-\delta}MF_6$ (M = Sb or Ta [74]) at 173 and 150 K, respectively, were reported. It was confirmed that these compounds are isostructural to the Hg_3AsF_6 compounds studied previously.[70,71]

Based on the comparison of the structures of three types of the above-considered compounds and taking into account the short contacts (2.985 Å) between the terminal atoms of the adjacent cations $(Hg_4)^{2+}$, it can be concluded that the structure of $Hg_4(AsF_6)_2$ is intermediate between the structure of $Hg_3(AsF_6)_2$, in which short contacts between the cations are absents, and the structure of $Hg_{3-\delta}AsF_6$, which contains infinite Hg_n chains and in which there are no discrete cations. Taking into account the high electrical conductivity of compounds containing infinite Hg_n chains, the authors [68] believed that the conductivity can occur along the zigzag chains in $Hg_4(AsF_6)_2$.

The preparation and investigation of gold-coloured crystals containing infinite Hg_n chains with compositions $Hg_{3-\delta}NbF_6$ and $Hg_{3-\delta}TaF_6$ led to the unexpected discovery of a new type of mercury compounds, which contain Hg_n layers, but differ from chain compounds.[75] If the gold-coloured crystals were not removed from the reaction mixture containing unconsumed mercury and $(Hg_3)^{2+}$ and $(Hg_4)^{2+}$ ions in the solution, these crystals were transformed over a period of time (from several hours to several months) into thin pliable silvery plates reminiscent of aluminium foil. The reaction performed in the cold (-35 °C) afforded silvery crystals without intermediate formation of gold-coloured crystals. Unlike the gold-coloured crystals, the silvery crystals have the exactly stoichiometric composition Hg_3MF_6 (M = Nb or Ta), which is determined by its close-packed structure. The crystals with this composition exhibit superconducting properties ($T_c = 7$ K).[64]

X-Ray diffraction studies of the Hg_3NbF_6 and Hg_3TaF_6 compounds revealed close-packed layers of the MF_6^- octahedra separated by hexagonal layers of the mercury atoms (Fig. 21).[75] Each mercury atom is surrounded by six nearest neighbours at distances of 2.90 Å within the Hg layer and by six fluorine atoms from the adjacent MF_6 layers at distances of 3.2 Å (three atoms from each adjacent layer). The mercury and fluorine atoms form the cubic close packing and the M atoms occupy 1/3 of the octahedral cavities between the fluorine atoms. The Hg—Hg distances in the mercury layers are longer than those in the chains, in which the mercury atoms are bound only to two neighbours, but are shorter than in elemental mercury, in which metal atoms have 10 or 12 neighbours. It should be noted that the silvery crystals were rapidly converted into the gold-coloured crystals in the presence of liquid SO_2 at 120 °C. Hence, it can be stated that there is a reversible structural transition between the chain and layered structures. However, the role of SO_2 in this transition is not entirely known (this transition does not occur at room temperature and below room temperature in the absence of SO_2).

The synthesis, structure and electrical properties of salts containing polyatomic $(Hg_3)^{2+}$ and $(Hg_4)^{2+}$ cations and compounds with chain ($Hg_{3-\delta}MF_6$, where M = As, Sb, Nb or Ta) and layered (Hg_3NbF_6 and Hg_3TaF_6) structures were considered in greatest detail in the study.[64]

In none of the known compounds containing $(Hg_2)^{2+}$ and $(Hg_3)^{2+}$ ions, these ions tend to bind to each other. The $(Hg_4)^{2+}$ ions in the compounds form zigzag chains through weak bonds. The limiting case is observed in the structures of $Hg_{3-\delta}MF_6$ ($\delta = 0.1$), (M = As, Sb, Nb or Ta) consisting of infinite chains, in which the oxidation state of mercury is close to $+1/3$ and the chains are virtually linear and uniform. The tendency of the ions to form chains, apparently, results from the low oxidation state and chains are formed if the charge on the mercury atom is lower than $\sim +1/2$. It should be noted that infinite linear chains of mercury atoms were found in β-Hg.[69] The layers of mercury atoms were observed in the graphite intercalation compound with composition $KHgC_4$.[76] Although the Hg—Hg distances in $KHgC_4$ are close to those in Hg_3NbF_6 (2.85 and 2.90 Å, respectively), the layers in these structures differ in that each mercury atom in Hg_3NbF_6 has 6 neighbours and the formal charge of $+1/3$, whereas each mercury atom in the intercalation compound has only three neighbours and the formal charge of 0.

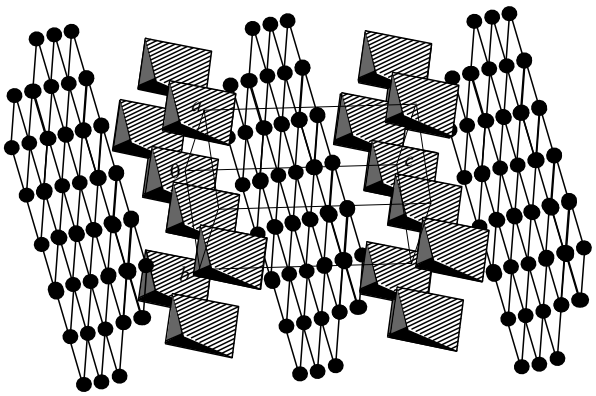


Figure 21. Hexagonal Hg_n layers in the structure of Hg_3NbF_6.

Therefore, analysis of the structures of mercury compounds with fluorine and MF_6^- anions shows the strict relationship between the value of the averaged formal charge on the mercury atom, the shortest Hg—F distances, the structure of the Hg_n^{x+} cation and the Hg—Hg distance in this cation. As the charge on the mercury atom decreases from $+1$ to $+1/3$, the shortest Hg—F distances increase from 2.133 in Hg_2F_2 to 3.2 Å in Hg_3NbF_6 and the sizes of the Hg_n^{x+} cation increase going from the finite and virtually linear Hg_n^{2+} groups ($n = 2-4$) to the infinite Hg_n chains and then to a two-dimensional close-packed layer of the mercury atoms. The Hg—Hg distances in this series of the cations increase from 2.51 to 2.90 Å.

V. Monovalent mercury compounds with organic ligands

Presently, 30 complex compounds with organic ligands containing $(Hg_2)^{2+}$ groups have been synthesised and structurally characterised. The principal crystallographic and crystal-chemical characteristics of these compounds are given in Table 1. Most organic ligands, which are constituents of the complexes under consideration, are shown in Fig. 22.

Many amines, including pyridine, cause disproportionation of the dimeric $(Hg_2)^{2+}$ cation

$$(Hg_2)^{2+} \longrightarrow Hg^{2+} + Hg^0.$$

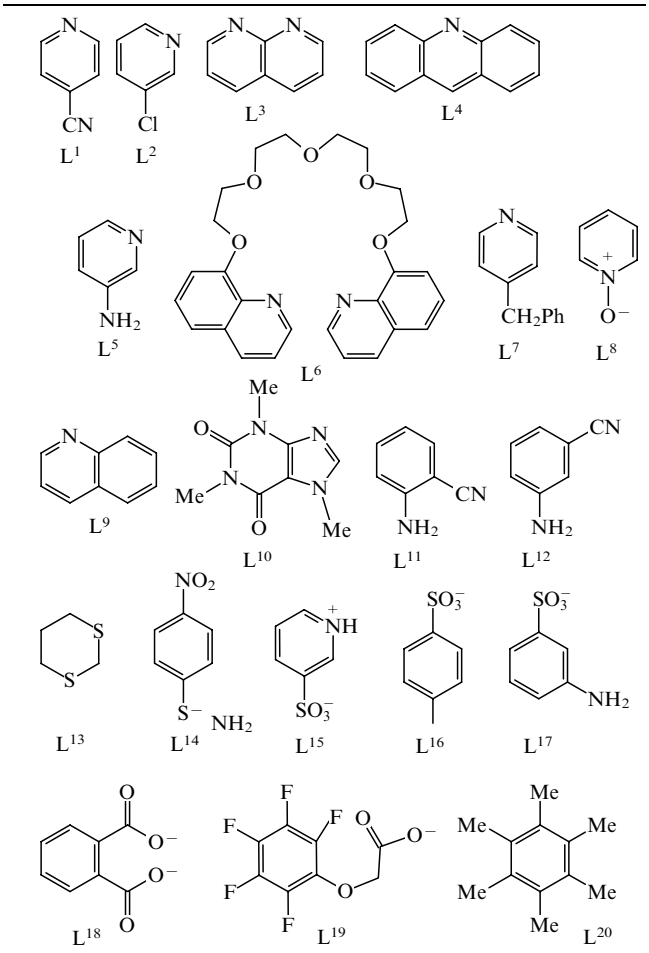


Figure 22. Types of organic ligands in monovalent mercury complexes.

The possibility of formation of stable monovalent mercury complexes with low-basicity nitrogen bases was confirmed for the first time by the detection of the $(Hg_2)^{2+}$ complex with aniline in solution.[77] Apparently, the introduction of an acceptor substituent at position 4 of the pyridine ring leads to a decrease in the donor ability of the nitrogen atom. Some substituted low-basicity pyridines and anilines also form stable $[Hg_2L_2]X_2$, complexes,[78] the basicity of the ligand depending on both the electronic and steric properties of the substituents. Structural study of the isolated $[Hg_2(L^1)_2](ClO_4)_2$ compound [79] demonstrated that the $(Hg_2)^{2+}$ ion can be covalently coordinated to the N-donor ligands through both mercury atoms.

The virtually linear N—Hg—Hg—N fragments (the Hg—Hg—N angles vary from 162.8 to 180°) were found in dimercury perchlorates with low-basicity N-containing organic ligands of the general formula $[Hg_2L_n](ClO_4)_2$ ($n = 2$);[79–83] the Hg—Hg and Hg—N bond lengths are in the ranges of 2.487–2.518 and 2.03–2.22 Å, respectively. The structures of the complexes contain the dimeric $[Hg_2L_2]^{2+}$ cations and the ClO_4^- anions. Noteworthy is the existence of nonbonded contacts between the mercury atoms of the $(Hg_2)^{2+}$ ions and the oxygen atoms of the ClO_4^- anions. The lengths of these contacts (2.93–3.13 Å) are somewhat larger than the sum of the van der Waals radii of the mercury and oxygen atoms (2.90 Å). The shorter Hg···O contacts were observed in the $[Hg_2(L^2)_2](ClO_4)_2$ (2.71 Å),[80] $[Hg_2(L^3)_2].(ClO_4)_2$ (2.79 Å)[81] and $[Hg_2(L^5)_2](ClO_4)_2$ (2.77 Å)[83] compounds. In the complex with acridine $[Hg_2(L^4)_2](ClO_4)_2$, the lengths of these contacts are 2.96 Å,[82] and hence one can say that only weak electrostatic interactions occur between the cations and the anions. The short Hg—N distance in the complexes with the ratio $(Hg_2)^{2+}:L = 1:2$ was found in $[Hg_2(L^3)_2](ClO_4)_2$.[81] The Hg—Hg distance (2.518 Å) in this compound is somewhat larger than those in the $[Hg_2(L^1)_2](ClO_4)_2$ (2.498 Å)[79] and $[Hg_2(L^2)_2](ClO_4)_2$ (2.487 Å)[80] complexes. The arrangement of the $[(Hg_2)^{2+}(L^1)_2]$ cations in the structure of the complex, which is analogous to the arrangement of the molecules in $Hg_2(NO_3)_2 \cdot 2H_2O$, is the so-called herringbone packing (see Fig. 2).[7,8] In the remaining complexes, the linear N—Hg—Hg—N fragments are primarily located parallel to one of the crystallographic axes.[80–83]

In the $[Hg_2(L^6)_2](ClO_4)_2$ complex [84] with the stoichiometry $(Hg_2)^{2+}:L^6 = 1:2$, the ligand is coordinated to the mercury atoms of the $(Hg_2)^{2+}$ pair through the nitrogen and oxygen atoms, the coordination environment about the mercury atoms being different. The environment about the Hg(1) atom is formed by the adjacent mercury atom (Hg—Hg, 2.506 Å), the nitrogen atom (2.20 Å) and two oxygen atoms (2.63 and 2.69 Å). The coordination about the Hg(2) atom involves the mercury, nitrogen (2.20 Å) and oxygen (2.66 Å) atoms. The remaining Hg···O(L^6) distances are in the range of 2.89–4.15 Å. The ClO_4^- anions are not coordinated to the metal atoms.

The coordination number of 3 is typical of the mercury atoms in the structures of the $Hg_2L_4(ClO_4)_2$ compounds. Thus, the dimercury perchlorate complex with 4-benzylpyridine (L^7) consists of the centrosymmetrical $[Hg_2(L^7)_4]^{2+}$ cations and the ClO_4^- anions, which are linked *via* weak Hg···O contacts (2.899 and 3.026 Å).[85] Without considering these contacts, the coordination about the mercury atoms is intermediate between planar-trigonal and the so-called T-shaped [86] (one of the Hg—Hg—N angles is close to 180°; Hg—Hg is 2.508 Å, Hg—N are 2.227 and 2.476 Å) (Fig. 23). It should be noted that the L^7 ligand possesses the highest basicity in the series of the above-mentioned N-donor ligands, which is manifested in the distortion of the T-shaped environment towards the planar-trigonal coordination. A comparison of the structural data on the dimercury complexes with sterically unhindered ligands, such as 4-cyanopyridine (L^1),[79] 3-chloropyridine (L^2)[80] and 4-benzylpyridine (L^7),[85] revealed an interesting correlation between the stereochemistry and the basicity of the ligands (pK_a is 1.86, 2.81 and 5.59, respectively).[85] There are weak contacts between the mercury atoms and the

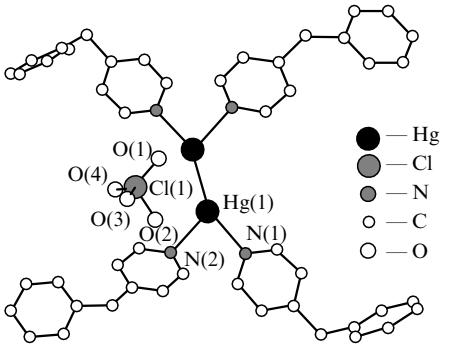


Figure 23. Molecular structure of $[Hg_2(L^7)_4](ClO_4)_2$.

oxygen atoms of the ClO_4^- anions in all three complexes regardless of the initial coordination of ligands in the axial positions with respect to the $(Hg_2)^{2+}$ pair. As the basicity of the above-mentioned ligands increases, the secondary coordination becomes more essential. In particular, the secondary Hg···L contacts [2.86 Å (O), 2.77 Å (O) and 2.476 Å (N)] become shorter and the Hg—Hg—L angles increase (100°, 109° and 118.4°), due to which the second ligand approaches the strong acceptor axial centre of the $(Hg_2L_2)^{2+}$ dimer. Correspondingly, the coordination is weakened, which is manifested in the increase in the Hg—N bond length (2.16, 2.21 and 2.23 Å). The deviation of the N—Hg—Hg—N fragment from linearity also increases (the N—Hg—Hg angles are 176.0°, 167.4° are 153.9°). Hence, it is evident that the deviation of the N—Hg—Hg—N fragments from linearity in stable dimercury complexes with N-donor ligands of the $[Hg_2L_n]_2X_2$ type ($n > 2$) is caused by the additional coordination of the metal atoms by more remote ligands.

The coordination polyhedra about the mercury atoms in the $[Hg_2(L^8)_4](ClO_4)_2$ compound are distorted tetrahedra formed by the mercury atom (Hg—Hg, 2.522 Å) and three oxygen atoms of the ligands (Hg—O, 2.197–2.558 Å).[87] An analogous coordination with the elongated Hg—O bonds, which is untypical of mercury atoms, was also found in Hg_2AgPO_4 (see Ref. 32) and in the mineral szymanskiite.[40] The remaining Hg···O contacts are longer than 2.78 Å. The $[Hg_2(L^8)_4]^{2+}$ dimers lie in the (010) plane. The distances between the adjacent dimers are 3.90 and 4.17 Å (Fig. 24). In addition, there is a rather long contact (2.96 Å) between the mercury atom and the oxygen atom of the ClO_4^- anion. Therefore, the structure of the $[Hg_2(L^7)_4](ClO_4)_2$ complex contains only discrete cations with the three-coordinate mercury

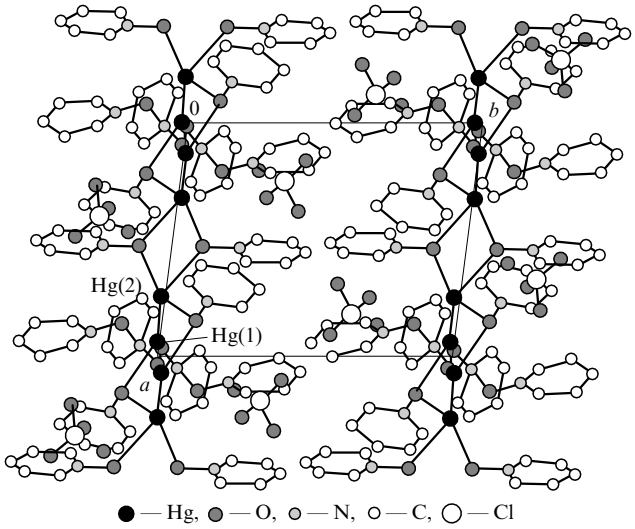


Figure 24. Projection of the structure of $[Hg_2(L^8)_4](ClO_4)_2$ onto the (001) plane.

atoms, whereas three of four ligands in the $[Hg_2(L^8)_4](ClO_4)_2$ complex act as bridges between the adjacent $(Hg_2)^{2+}$ cations.[85]

The compound $Hg_2(Ph_2Se)_4(ClO_4)_2$ exists in two forms, *viz.*, in the 'yellow'[88] and 'red'[89] forms. The 'yellow' complex contains the centrosymmetrical $[(Ph_2Se)_2Hg_2(Ph_2Se)_2]^{2+}$ cations with positively charged trivalent selenium atoms.[88] One of the oxygen atoms of each ClO_4^- anion is bound to the $(Hg_2)^{2+}$ group. Each mercury atom has the trigonal environment formed by the mercury atom (Hg—Hg, 2.558 Å), the selenium atom (Hg—Se, 2.70 Å) and the oxygen atom of the ClO_4^- anion (Hg—O, 2.705 Å). In addition, there is a contact between the mercury atom and the selenium atom (2.80 Å), which completes the coordination about the mercury atom to a distorted tetrahedron. The observed Hg—Hg distance belongs to the longest distances found in the $(Hg_2)^{2+}$ groups. The value of one of the Hg—Hg—Se angles (141°) indicates that the linear coordination about the mercury atom is distorted upon addition of the second diphenyl selenide group. Correspondingly, the Hg—Se distance is 2.70 Å at the Hg—Hg—Se angle of 141°, while this distance increases to 2.80 Å at the angle of 116°. In the centrosymmetrical molecule of the 'red' form, the central Hg_2Se_4 fragment is planar.[89] The fourth coordination site at the mercury atom is occupied by an oxygen atom of the ClO_4^- anion (Hg—Hg, 2.554 Å; Hg—Se, 2.653 and 2.918 Å; Hg—O, 2.626 Å; the Hg—Hg—Se angle is 151.9°). Therefore, the 'yellow' and 'red' forms of the $Hg_2(Ph_2Se)_4.(ClO_4)_2$ compound are characterised by the different structures of the Hg_2Se_4 fragments and the different molecular packings in the crystals.

In the $Hg_2[(Ph_3PO)_6](ClO_4)_2$ complex with the stoichiometry $(Hg_2)^{2+}:L = 1:6$, the coordination environment around each mercury atom is a tetrahedron formed by three ligands and the adjacent mercury atom of the $(Hg_2)^{2+}$ pair. As a result, the discrete complex cation is formed (Hg—Hg, 2.522 Å; Hg—O, 2.29–2.43 Å).[90] The ClO_4^- anions are not involved in the coordination sphere about the mercury atoms. In this complex, the mercury atoms have the so-called umbrella-type coordination formed by the oxygen atoms of the ligands with elongated Hg—O bonds. This coordination is analogous to that found in $Hg_2Ag.PO_4$,[32] szymanskiite[40] and the $[Hg_2(L^8)_4](ClO_4^-)_2$ complex.[87]

It should be noted that compounds of the $Hg_2L_2X_2$ type contain discrete dimeric cations, in which each mercury atom is linearly coordinated. The Hg—L bonds are in the range of 2.03–2.35 Å and the X anions are located at large distances from the mercury atoms (2.8–3.0 Å). In the compounds with composition $Hg_2L_4X_2$, the coordination about the mercury atoms is intermediate between linear and tetrahedral. Besides, data on polymeric complexes with bridging N-containing L ligands, which are analogous to those found in $[Hg_2(L^8)_4](ClO_4)_2$ with O-containing ligands, are lacking.[87] Only in the $Hg_2[(Ph_3PO)_6].(ClO_4)_2$ compound, is the coordination environment about the mercury atoms a tetrahedron.[90]

The existence of the stable mercury complex with 1,10-phenanthroline (Phen) confirms the possibility of complexation of dimercury ions with low-basicity amines. The $Hg_2Phen(NO_3)_2$ complex with the ratio $(Hg_2)^{2+}:L = 1:1$ has a layered structure. The discrete $[Hg_2(Phen)]^{2+}$ cations are separated by layers of the NO_3^- anions.[91] The mercury atoms have different coordinations. Thus, the Hg(1) atom has four nearest neighbours; the tetrahedron is formed by the Hg(2) atom (Hg—Hg, 2.516 Å), the nitrogen atoms of the phenanthroline molecule (2.30 and 2.48 Å) and the oxygen atom of NO_3^- anion (2.59 Å). Another oxygen atom of the NO_3^- anion is located at a distance of 2.91 Å. The nearest environment about the Hg(2) atom is formed by the Hg(1) atom and the oxygen atom of the NO_3^- anion. The remaining oxygen atoms are at distances of 2.75–2.95 Å. Therefore, the 1,10-phenanthroline molecule is bound to only one mercury atom of the $(Hg_2)^{2+}$ pair. Attempts to isolate the compound with composition $Hg_2(Phen)_2(NO_3)_2$ failed.

In compounds with the stoichiometry $Hg_2^{2+}:L = 1:2$ $[Hg_2(L^9)_2](NO_3)_2$ and $[Hg_2(L^{10})_2](NO_3)_2$, the nearly linear —N—Hg—Hg—N— groups were found with the Hg—Hg distances of 2.551[92] and 2.517 Å[93] and the Hg—N distances of 2.168 Å[92] and 2.193 Å.[93] The shortest distances to the oxygen atoms of the NO_3^- anions are 2.696–3.000 Å. The authors[93] believed that the contacts, characterised by these lengths, play a decisive role in the molecular packing of the complex.

The structures of $[Hg_2(L^{11})_2](NO_3)_2$ (see Ref. 94) and $[Hg_2(L^{12})_2](NO_3)_2$ (see Ref. 95) contain the nearly linear —N—Hg—Hg—N— groups (Hg—Hg, 2.518 Å[94] and 2.524 Å[95]; and Hg—N, 2.233 Å[94] and 2.209 Å[95]). Taking into account the Hg···O distance (2.659 Å), the coordination about the mercury atoms is close to T-shaped.[94] In addition, each mercury atom has contacts with the oxygen atom of the NO_3^- anion (Hg···O, 2.769 Å) and the nitrogen atom of the nitrile group (2.906 Å). The NO_3^- anions are involved in hydrogen bonding with the NH_2 groups of the adjacent molecules (N···O, 2.88 and 3.02 Å) through the noncoordinated and coordinated oxygen atoms to form chains along the [100] direction. These chains are linked in layers parallel to the (010) plane through the $Hg—N_{CN}$ interactions (2.906 Å).

The mercury atoms in the dimeric cation of the $Hg_2(L^{13})_2(NO_3)_2$ complex have different coordinations. Thus, the Hg(1) atom is coordinated to the Hg(2) atom at a distance of 2.541 Å and, in addition, forms a covalent bond with the sulfur atom of the ligand (2.49 Å). The S—Hg—Hg—S fragment is virtually linear (the Hg—Hg—S angle is 173.5°).[96] The coordination environment about the Hg(2) atom is more complicated. The nearest environment involves the oxygen atoms of two NO_3^- groups (2.516 and 2.651 Å) along with the sulfur atom of the ligand (2.584 Å). In addition, there are Hg···O contacts between the Hg(1) atom and the NO_3^- groups (2.773 and 2.820 Å). The L^{13} ligands serve as bridges between the mercury pairs. In the structure, the $-L^{13}-(Hg_2)^{2+}-L^{13}-$ chains are extended parallel to the [101] direction.

The $Hg_2(L^{14})_2(NO_3)_2$ compound contains the $[-(Hg_2)^{2+}-S-(Hg_2)^{2+}-]$ chains with the three-coordinate sulfur atoms and the NO_3^- anions (Hg—Hg, 2.548 Å; Hg—S, 2.488 and 2.477 Å; the Hg—Hg—S angles are 161.9 and 163.8°);[97] Hg···O contacts (2.64–3.14 Å) are observed. The O(3) atom of the NO_3^- anion acts as a bridge [Hg(1)—O(3), 2.652Å; and Hg(2)—O(3), 2.636 Å], completes the coordination about the mercury atom to T-shaped and links the chains in corrugated ribbons along the *b* axis (Fig. 25).

In the crystal of the complex $Hg_2(L^{15})_2(H_2O)_2$, the molecules exist as zwitter-ions with the formal positive charge on the nitrogen atom and the negative charge on the sulfate ion.[98] The N—Hg—Hg—N fragment has a nearly linear configuration. The

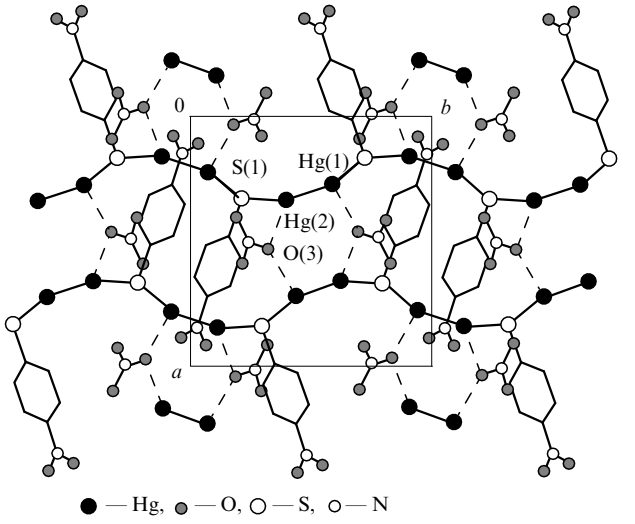


Figure 25. Corrugated ribbons extended along the *b* axis in the crystal structure of $Hg(L^{14})_2(NO_3)_2$.

Hg—Hg bond is rather short (2.494 Å). The mercury atoms form additional contacts with the oxygen atoms of the water molecules (2.621 Å) and of the SO_3^- groups of the L^{15} ligand (2.680 Å).

The structures of $Hg_2(L^{16})_2$, $Hg_2(L^{17})_2$ and $Hg_2(L^{17})_2(H_2O)_2$ contain the centrosymmetrical complexes, in which the mercury atoms are coordinated by the nitrogen atoms to form the nearly linear [—N—Hg—Hg—N—] fragments.[99] The Hg—Hg bond lengths are 2.500, 2.515 and 2.522 Å in $Hg_2(L^{16})_2$, $Hg_2(L^{17})_2$ and $Hg_2(L^{17})_2(H_2O)_2$, respectively. The Hg—N bond lengths are virtually identical (the average value is 2.19 Å). In the $Hg_2(L^{16})_2$ and $Hg_2(L^{17})_2(H_2O)_2$ compounds, the $(Hg_2)^{2+}$ pairs are rotated with respect to each other by 78 and 68°, respectively. In $Hg_2(L^{17})_2$, these pairs are parallel to each other. There are weak Hg···O interactions, whose lengths are close to the sum of the van der Walls radii. Thus, there are contacts with three oxygen atoms of two ligand molecules (2.67, 2.92 and 2.99 Å) in the $Hg_2(L^{16})_2$ compound, contacts with the oxygen atoms of the SO_3^{2-} group (2.68 Å) in $Hg_2(L^{17})_2$ and contacts with the oxygen atoms of the ligand (2.711 Å) and of the water molecule (2.715 Å) in $Hg_2(L^{17})_2(H_2O)$,. The $Hg_2(L^{16})_2$ and $Hg_2(L^{17})_2(H_2O)_2$ complexes are linked in layers and the $Hg_2(L^{17})_2$ complexes are linked in chains through the ligand molecules (Fig. 26). In the $Hg_2(L^{17})_2$ and $Hg_2(L^{16})_2$ compounds, the oxygen atoms of the SO_3^{2-} groups are involved in intermolecular hydrogen bonding with the NH_2 groups (N···O, 2.85–3.06 Å). In $Hg_2(L^{17})_2(H_2O)_2$, the oxygen atoms are involved in hydrogen bonding with the water molecules (O···O, 2.777 and 2.784 Å).

The nearest environment about each mercury atom of *o*-phthalate $Hg_2(L^{18})_2$ involves the oxygen atom. In this case, the virtually linear O—Hg—Hg—O fragments are formed (Hg—Hg, 2.519 Å; and Hg—O, 2.16 and 2.08 Å). The $(Hg_2)^{2+}$ pairs link the *o*-phthalate groups to form infinite zigzag chains.[100] In the unit cell, eight crystallographically equivalent chains are linked in pairs and are located parallel to the *b* axis, *i.e.*, along the longest crystallographic axis.

The typical pseudosymmetrical dimer with the Hg—Hg bond (2.514 Å) was also found in the $[Hg_2(L^{19})_2]_n$ compound.[101] The L^{19} ligand is involved in one strong bond (Hg—O, 2.13 Å) and one weak intermolecular Hg···O bond (2.63 Å) through which the $(Hg_2)^{2+}$ dimers are linked in chains along the [100] direction. Taking into account this bond, the coordination about the mercury atom is close to T-shaped.

The crystal structure of $Hg_2(CF_3CO_2)_2$ consists of discrete Hg_2L_2 molecules. The [—O—Hg—Hg—O—] fragments are virtually linear (Hg—Hg, 2.505 Å; and Hg—O, 2.14 Å).[102] The additional Hg···O distances (2.81 and 2.88 Å) have no substantial effect on the characteristic coordination about the mercury atom. The $Hg_2(CF_3CO_2)_2$ molecules are linked in corrugated ribbons along the [001] direction through intermolecular Hg···O bonds (2.64 Å) (Fig. 27). Taking into account this contact, the coordination about the mercury atom is T-shaped. In the crystal structure, the ribbons are linked in layers *via* F···F contacts (2.78–3.12 Å).

In the $Hg_2[C(CN)_3]_2$ complex,[103] the $(Hg_2)^{2+}$ ions form three elongated bonds with the nitrogen atoms of the CN^- groups (Hg—N, 2.287–2.508 Å) along with the Hg—Hg bond (2.506 Å). This coordination is analogous to the coordination about the mercury atoms of the $(Hg_2)^{2+}$ pairs mentioned in several studies.[32, 40, 87, 90] The centres of the $(Hg_2)^{2+}$ pairs coincide with the inversion centres. The ligands are bridging and tridentate. All the nitrogen atoms of each ligand are involved in coordination about different mercury atoms to form a three-dimensional framework (Fig. 28).

In the centrosymmetrical cation of the $Hg_2(C_7HN_4)_2$ complex, the mercury atoms have the distorted trigonal environment formed by the adjacent mercury atom and the nitrogen atoms of two carbanions of the ligand (Hg—Hg, 2.503 Å; Hg—N, 2.207 and 2.560 Å; the Hg—Hg—N angles are 162.2 and 116.5°).[104] The cations are linked in chains along the *a* axis through the ligands. The mercury atoms form weak Hg···N contacts (2.753 and 2.935 Å) through which the chains are linked in layers (Fig. 29).

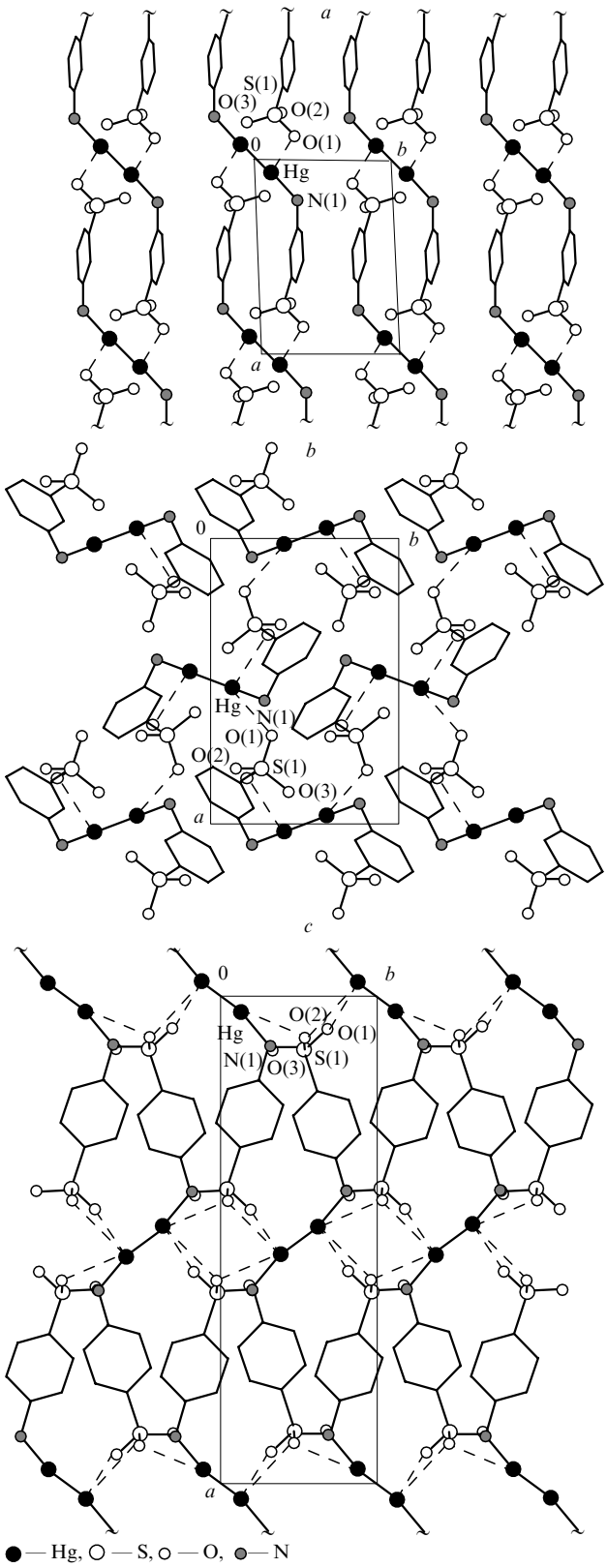


Figure 26. Molecular packings in the structures of the complexes: (*a*) $Hg_2(L^{16})_2$; (*b*) $Hg_2(L^{17})_2(H_2O)_2$; and (*c*) $Hg(L^{17})_2$.

The rather unusual complex with hexamethylbenzene with composition $[Hg_2(L^{20})_6](AlCl_4)_2 \cdot C_7H_8$ was described.[105] The hexamethylbenzene L^{20} ligands are asymmetrically coordinated to the $(Hg_2)^{2+}$ dimer in the η^2 fashion. The distances from the mercury atoms to the planes of the ligands are 2.356 and 2.367 Å. In the crystal structure, the complexes with the Hg—Hg bonds

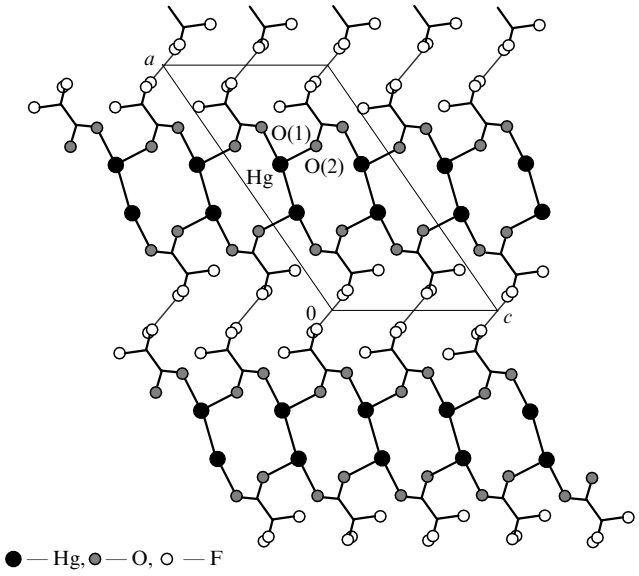


Figure 27. Crystal structure of $Hg_2(CF_3CO_2)_2$. The F···F contacts are indicated by dashed lines.

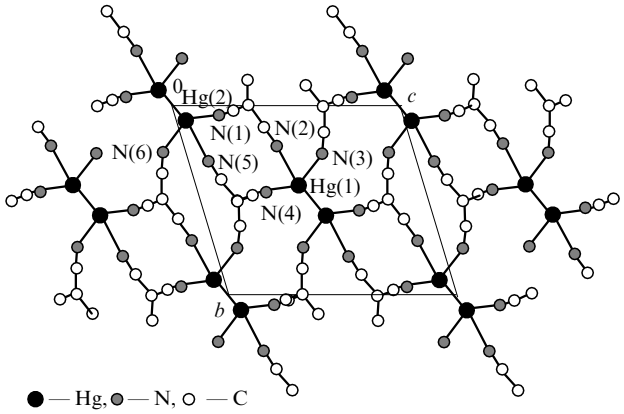


Figure 28. Projection of the crystal structure of $Hg_2[C(CN)_3]_2$ onto the (100) plane.

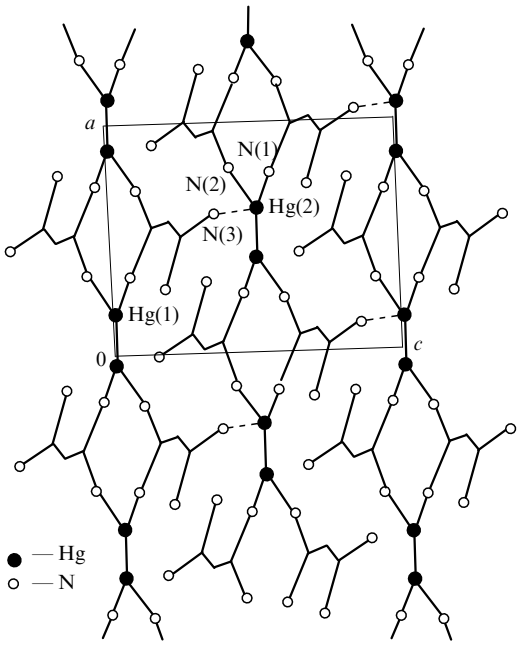


Figure 29. Layered structure of the $Hg_2(C_7HN_4)_2$ complex.

(2.515 Å) are located parallel to the *b* axis. The structure contains also distorted $AlCl_4$ tetrahedra. The shortest Hg···Cl distances are 3.10 and 3.12 Å.

Analysis of the Hg—Hg and Hg—L bonds in the monovalent mercury complexes with organic ligands demonstrates that there is no strict correlation between these parameters, as in inorganic compounds containing mercury in low oxidation states. The Hg—Hg distances vary from 2.487 to 2.558 Å, which is in good agreement with the distances observed in the crystal structures of inorganic compounds. In the complexes of the $Hg_2L_nX_2$ type (n = 2, 4 or 6) with $X = ClO_4^-$ (see Refs 79–90), the anions have no substantial effect on the Hg—Hg bond length and are involved only in nonbonded interactions with the metal atoms, whereas the oxygen atoms of the anions in the complexes with $X = NO_3^-$ (see Refs 91–97) complete the coordination about the mercury atoms of the $(Hg_2)^{2+}$ pairs (Hg···O, 2.516–2.769 Å). In the $Hg_2(L^{15})_2(H_2O)_2$ (see Ref. 98) and $Hg_2(L^{17})_2(H_2O)_2$ (see Ref. 99) complexes, the water molecules are involved only in formation of additional bonds with the mercury atoms of the $(Hg_2)^{2+}$ pairs or in hydrogen bonding with the atoms of the ligands, whereas inorganic aqua complexes contain the aqua $[H_2O—Hg—Hg—OH_2]^{2+}$ cations. In the molecular complexes of the Hg_2L_2 type, the Hg—Hg bond lengths vary from 2.500 to 2.519 Å.[99–104] The complexes are linked in chains and layers through additional Hg···L contacts, as in inorganic monovalent mercury compounds. The coordination environment about the mercury atoms is formed primarily by atoms of organic ligands. In most compounds, anions are not coordinated to the metal atoms (the coordination number of the mercury atoms is 2).[79–83] When the coordination number of Hg increases to 3 or 4 taking into account the contacts with the anions, the structures can be described as chain, layered[9] and framework.[4–102, 104, 105]

VI. Mercury-containing transition metal clusters

Presently, the data on a series of mercury-containing transition metal clusters containing either $(Hg_2)^{2+}$ pairs or more complicated cluster Hg_n groups are available. The principal crystallographic and crystal-chemical data for selected mercury-containing clusters are given in Table 1. In this section, we consider the mercury-containing clusters with the Hg—Hg bond lengths varying in the range of 2.65–3.27 Å.

The structure of the $Hg_2Co_2[N(CH_2CH_2PPh_2)_3]_2(THF)$ cluster consists of the discrete $\{[N(CH_2CH_2PPh_2)_3]Co(Hg—Hg)Co[N(CH_2CH_2PPh_2)_3]\}$ molecules and the tetrahydrofuran molecules located between the complex molecules. Two $Co[N(CH_2CH_2PPh_2)_3]$ fragments are linearly bonded through the $(Hg_2)^{2+}$ ion (Fig. 30) so that the four metal atoms of the —Co—Hg—Hg—Co— fragment are coplanar (the Co—Hg—Hg angles are 179.7 and 178.4°).[106] The two-coordinate mercury atoms are shielded from additional bonding with the Ph rings of the $[N(CH_2CH_2PPh_2)_3]$ ligands. The Hg—Hg distance (2.651 Å) is somewhat larger than those in the dimercury complexes with organic ligands. The shortest contact between the carbon atoms of the Ph rings and the mercury atoms is 3.48 Å.

The study of the compound $\{Hg_2Pt_6[Ph_2P(CH_2)_6PPh_2]_3.(C_8H_9NC)_6\}\cdot 2C_6H_6$ demonstrated that the $(Hg_2)^{2+}$ pair is inserted into the trigonal antiprismatic cage of the platinum atoms.[107] Two Pt_3 triangles are tightened by three $[Ph_2P(CH_2)_6PPh_2]$ ligands. Six isocyanide molecules act as bridging ligands in each triangular unit. The Hg—Hg distance (2.872 Å) is larger than the analogous distances in monovalent mercury compounds with organic ligands but is somewhat shorter than the distances between the metal atoms in metallic mercury.[69]

The structural studies of mercury-containing metal carbonyl compounds demonstrated that, as in compounds containing linear Hg_n chains (n = 3 or 4), the Hg—Hg distances are in the range of 2.5–2.8 Å. This is indicative of a strong covalent bond, which is formed due to the overlap of the linear *sp*-hybridised orbitals. In the cases where other atoms, for example, transition

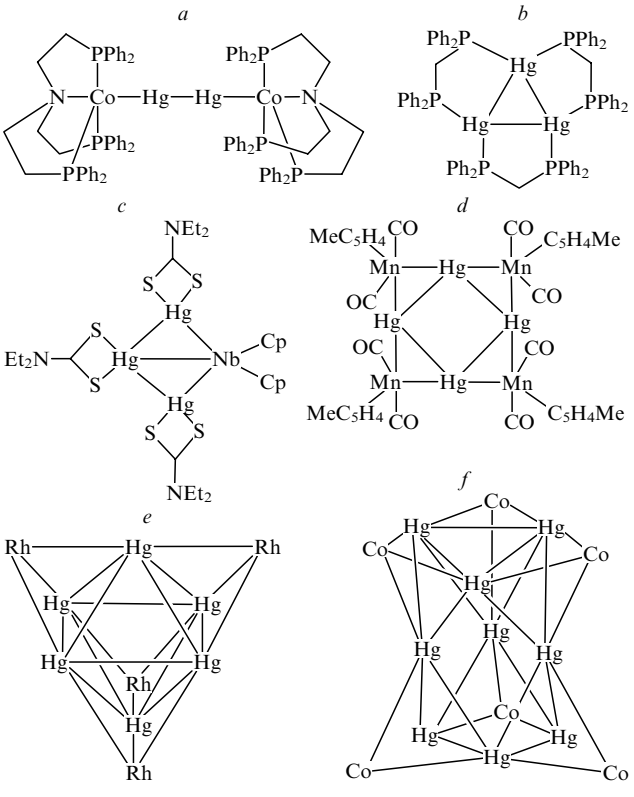


Figure 30. Schemes of the structures of mercury-containing transition metal clusters: (*a*) $Hg_2Co_2[N(CH_2CH_2PPh_2)_3]_2(THF)$; (*b*) $\{Hg_3[(Ph_2P)_2CH_2]_3\}(SO_4)_2 \cdot 1.5H_2O$; (*c*) $[Nb(\eta\text{-}C_5H_5)_2\{HgS_2CN.(C_2H_5)_2\}_3]$; (*d*) $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2Hg]_4$; (*e*) $[(C_{12}H_{36})_3Rh]_4Hg_6$; and (*f*) $[Hg_9Co_6(CO)_{18}] \cdot 2(C_3H_6O)$.

metals (M), are involved in the Hg—Hg bond, the distances in the clusters increase to 3.2 Å.

In the $[(Ph_3P)_2N]_2[Hg_2Os_{18}(CO)_{42}C_2]$ cluster, the vertices of the Os triangles are linked through the mercury atoms to form the $Os_9C(CO)_{21}$ units.[108] The molecule is centrosymmetrical with respect to the midpoint of the Hg—Hg bond. The Hg—Hg distance is 2.744 Å, whereas the Hg—Hg bond in the $[(Ph_3P)_2N]_4[Hg_2(Os_{18}(CO)_{42}C_2](CH_2CH_2)$ cluster,[109] which contains the framework of the metal atoms with a similar structure, is somewhat longer (2.820 Å).

The triangular $(Hg_3)^{4+}$ cluster containing the mercury atoms in the oxidation state of +4/3 was found in the $\{Hg_3[(Ph_2P)_2CH_2]_3\}(SO_4)_2 \cdot 1.5H_2O$ compound.[110] Each mercury atom is bound to the bridging $(Ph_2P)_2CH_2$ ligands. In addition, two SO_4^{2-} anions form weak contacts with the mercury atoms. The Hg—Hg distances are 2.763, 2.764 and 2.802 Å, which are comparable with the analogous distances in the triangular groups observed in terlinguaite,[44] kuznetsovite[60] and $Hg_9As_4O_{16}$.[62]

In the $[(Ph_3P)_2N]_2[Ru_{18}Hg_3(C)_2(CO)_{42}] \cdot CH_2Cl_2$ cluster, the mercury triangle links two tricapped octahedral $[Ru_9(CO)_{21}C]$ fragments (Hg—Hg, 2.919 and 2.922 Å; Hg—Ru, 2.640–2.734 Å).[111] It should be noted that the Hg—Hg distances are virtually equal to the corresponding distances in metallic mercury.[69] In the solid state, the $[Ru_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ dianion has the symmetry C_3. The average angle of rotation of the central Hg_3 triangle with respect to the two adjacent Ru_3 triangles is 30°. The short Hg···C_{CO} contacts (the average length is 2.64 Å) are present in the structure.

An analogous Hg_3 unit links two $[Os_9(CO)_{21}C]$ fragments in the $[(Ph_3P)_2N]_2[Hg_3Os_{18}(CO)_{42}C_2] \cdot CH_2Cl_2$ cluster, the mercury triangle (Hg—Hg, 2.919–2.931 Å) being disordered.[112] Note that the Cd_3 triangle with the average Cd—Cd bond length of 2.980 Å was found in the structurally related $[\mu_3\text{-}Co(CO)_3]Cd_3\{\mu\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_3(THF)_3$ cluster.[113]

A series of Hg-containing metal clusters containing the heteronuclear triangular MHg_2 fragment were studied. The $Hg_2Ag[(Ph_2P)_2CH_2]_3(CF_3SO_3)_3$ cluster contains the Hg_2Ag triangle all vertices of which are bound to the $[(Ph_2P)_2CH_2]$ bridging ligands.[114] The Hg—Hg (2.660 Å) and Hg—Ag (2.805 and 2.853 Å) distances are close to those found in $AgHg_2PO_4$.[32] The mercury and silver atoms have an approximately planar-square coordination formed by two metal atoms and two phosphorus atoms.

In the examples of mercury-containing transition metal clusters considered below, the Hg—Hg bonds (2.883–3.274 Å) approximate the distances in metallic mercury. Therefore, the mercury—transition metal bonds in these clusters prevail.

The rather unusual nearly planar Hg_3Nb unit, which is located in the equatorial plane of the wedge-shaped Cp_2Nb sandwich, was found in the organometallic $[Nb(\eta\text{-}C_5H_5)_2\{HgS_2CN(C_2H_5)_2]_3$ cluster.[115] The dihedral angle between the NbHg(1)Hg(2) and NbHg(2)Hg(3) triangles in this complex is ~5°. The Hg—Hg bond lengths (2.883 and 2.901 Å) are indicative of a rather strong interaction between the adjacent mercury atoms. The Hg—Nb distances vary from 2.777 to 2.808 Å. The cluster molecules are linked in dimeric units through the weak Hg···S bonds [Hg(2)—S(11), 3.39 Å].

The organometallic $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2Hg]_4$ compound[116] contains the eight-membered Mn_4Hg_4 metallocycle in which four mercury atoms form a planar square with the Hg—Hg distances of 2.888 Å. The four-membered virtually planar Hg_4 ring (the Hg—Hg—Hg bond angle is 90°) was also found in the $[(\eta^5\text{-}C_5H_5Re(CO)_2Hg]_4$ cluster with an analogous structure.[117] The rhenium atoms are alternately located above and below the plane of the mercury square. The average angle of bend of the angular HgReHg fragments is 19.0°. The slight shortening of the Hg—Hg bonds (2.92 Å) compared to the distances in metallic mercury (2.99 Å) is indicative of the metal—metal interaction in the Hg_4 ring of the cluster. The authors believed that the distortion of the linear coordination of the mercury atoms (the Re—Hg—Re angle is 158.8°) is also evidence in favour of the Hg—Hg interaction. The observed eight-membered ring system is similar to that found previously in $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2Hg]_4$.[116] It should be noted that the Hg—M bonds are substantially shorter than the Hg—Hg distances in the above-described compounds [2.64 Å (Mn) and 2.74 Å (Re)].

The octahedra of six mercury atoms were observed in two clusters, *viz*., in $[(C_{12}H_{36})_3Rh]_4Hg_6$ (see Ref. 118) and $[(C_8H_{18}P)_2Pt]_4Hg_6$ (see Ref. 119). In the molecular structures of both compounds, the Rh and Pt atoms act as 'caps,' which complete the faces of the Hg_6 octahedra to form the heteroatomic Hg_6M_4 tetrahedron. The Hg—Hg bond lengths in the nearly regular mercury octahedra are in the ranges of 3.129–3.149[118] and 3.081–3.274 Å.[119] The Hg—Rh and Hg—Pt distances are in the ranges of 2.690–2.724 and 2.671–2.876 Å, respectively.

In the $[Hg_9Co_6(CO)_{18}] \cdot 2(C_3H_6O)$ cluster,[120] the structural unit containing nine mercury atoms was found. The framework of the metal atoms can be described as a distorted Co_6Hg_9 trigonal prism with the cobalt atoms occupying all vertices and the mercury atoms being located in the midpoints of the edges. The distances between the mercury atoms located in the centres of the triangular bases of the prism vary from 3.065 to 3.138 Å, whereas the distances from these atoms to the mercury atoms located in the midpoints of the edges of the prism, which link two bases, are somewhat longer (3.086–3.198 Å). The authors[120] believed that the Hg—Co interaction (2.521–2.609 Å) is the governing factor in the formation of the framework of the metal atoms.

The nature of the Hg—Hg interactions in the clusters of this type is still unclear. In the review,[121] the structures of transition metal clusters with mercury atoms were considered and an attempt was made to explain the nature of the Hg—Hg and Hg—M bonds. The structural studies of transition metal clusters

revealed the existence of the linear M—Hg—M units containing two-coordinate mercury atoms. The clusters can be divided into two types, *viz*., two-dimensional clusters in which mercury atoms form polygons {for example, a triangle in $(C_{36}H_{30}NP_2)_2.[Hg_3Os_9(CO)_{21}C_2]\cdot CH_2Cl_2$ (see Ref. 112) or a square in $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2Hg]_4$ (see Ref. 116)}, and three-dimensional clusters in which mercury atoms form polyhedra {for example, an octahedron in $[(C_{12}H_{36})_3Rh]_4Hg_6$ (see Ref. 118) and $[(C_8H_{18}P)_2Pt]_4Hg_6$ (see Ref. 119) or a tricapped trigonal prism in $[Hg_9Co_6(CO)_{18}]\cdot 2(C_3H_6O)$ (see Ref. 120)}. The mercury atoms in these clusters are characterised by the linear *sp* configuration of the metal—metal bonds and the involvement in the secondary Hg···Hg interactions (2.89–3.15 Å). Note that in the compounds considered in Refs 115–120, the bonds between the mercury atoms and the transition metal atoms are, apparently, determining. The Hg—Hg bond lengths (2.65–3.27 Å) are intermediate between the shortened bond lengths found in inorganic and complex compounds of monovalent mercury (2.46–2.59 Å) and the van der Waals $Hg^{2+}\cdots Hg^{2+}$ contacts (3.41 Å), which exist, for example, in polymercurated organic derivatives $R(HgX)_n$.[122–124]

VII. Conclusion

In the present review, the data on the crystal structures of inorganic and complex compounds of mercury in low oxidation states and on some mercury-containing transition metal clusters containing the $(Hg_2)^{2+}$ pairs and the Hg_n groups are summarised. The Hg—Hg and Hg—X bonds (X = O, N, S or Se) are analysed and the modes of coordination of the mercury atoms in the mercury pairs and cluster groups are considered.

The crystal chemistry of monovalent mercury compounds is similar to the crystal chemistry of divalent mercury compounds. The ability of the mercury atom to form linear X—Hg—X fragments is retained. However, the *sp*-bonds in the X—Hg—Hg—X groups are not necessarily exactly collinear. Interestingly, the bonds between the mercury atoms of the $(Hg_2)^{2+}$ pair and the X atom are longer (the average length is 2.14 Å) than the Hg—X distances in divalent mercury compounds (the average length is 2.06 Å). The environment about the mercury atoms in the $(Hg_2)^{2+}$ pairs is generally formed by two X atoms. However, the coordination of the pair may be completed by atoms located at larger distances. The instances of the nonlinear coordination about the atoms of the $(Hg_2)^{2+}$ dimers by three X atoms (X = O or N) with the longer Hg—X bonds are mentioned. The Hg—Hg bond lengths in inorganic and complex compounds of formally monovalent mercury vary from 2.46 to 2.59 Å. An increase in the Hg—Hg bond length is observed in the linear $(Hg_4)^{2+}$ groups (2.59–2.63 Å), infinite Hg_n chains (2.64–2.67 Å), $(Hg_3)^{4+}$ triangles (2.60–2.70 Å) and transition metal clusters containing $(Hg_2)^{2+}$ pairs, $(Hg_3)^{4+}$ triangles and Hg_n groups.

In mixed-valence compounds, the tendency of mercury-oxygen groups to polymerisation, which is typical of divalent mercury, is retained. Pairs of formally monovalent mercury atoms form linear $O-(Hg_2)^{2+}-O$ groups, which, in turn, form 10-, 12-, 14-, 16- and 22-membered rings in combination with each other and with the linear $O-Hg^{2+}-O$ fragments. The rings are linked in different fashions to form two-dimensional planar or corrugated networks, layers or frameworks. The structures with the 14-membered $\{[(Hg_2)^{2+}]_2(Hg^{2+})_4O_6\}$ rings are of frequent occurrence.

In compounds containing polyatomic groups of mercury atoms, the description of the coordination polyhedra about individual mercury atoms is arbitrary because these polyhedra are substantially distorted due to the presence of the strong Hg—Hg bond. In these cases, it is worthwhile from the crystal-chemical standpoint to consider this series of structures as containing the overall complex Hg_n cations (n = 2 or 3) with the coordinates of the geometric centres of the complexes and to describe the coordination environment about the Hg_n^{x+} cation as a whole.

In the structures of mercury compounds with fluorine and MF_6^- anions, the relationships between the value of the averaged formal charge on the mercury atom, the shortest Hg—F distances, the structure of the Hg_n^{x+} cation and the Hg—Hg distance in this cation are found. As the charge on the mercury atom decreases from +1 to +0.33, the Hg—F distance increases from 2.13 in Hg_2F_2 to 3.2 Å in Hg_3NbF_6 and the sizes of the Hg_n^{x+} cations increase in the series from the finite nearly linear groups to infinite Hg_n chains and planar close-packed layers of mercury atoms. The Hg—Hg distances in these cations vary from 2.51 to 2.90 Å.

Analysis of the structures of inorganic monovalent mercury compounds revealed no substantial effect of the mercury atoms of the $(Hg_2)^{2+}$ pair on the bond lengths in the anions, such as ClO_4^-, SO_4^{2-}, SeO_4^{2-}, PO_4^{3-} and NO_2^-, whereas an elongation of one of the bonds with the participation of the oxygen atom, which is bound to the mercury atom of the $(Hg_2)^{2+}$ pair, is observed in compounds with the AsO_4^{3-} and BrO_3^- anions. The NO_3^- anion rather often completes the coordination environment about the mercury atom through contacts of 2.45–2.88 Å and can act as a bridging ligand. In monovalent mercury complexes with organic ligands, the ClO_4^- anions are involved only in nonbonded interactions with the mercury atoms of the $(Hg_2)^{2+}$ pairs, while the function of the NO_3^- anions is analogous to that in inorganic monovalent mercury compounds.

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