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Studies on Sulphates, Selenates and Chromates of Mercury(II)

KARIN AURIVILLIUS and BIRGITTA MALMROS

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

For some mercury(II)salts containing tetrahedral anions (Table 2) the cell edges, cell contents and probable space groups are given.

Investigations of the crystal chemistry of mercury(II), which have been made at this Institute, have revealed that infinite —O—Hg—O— chains are fundamental constituents in a number of phases comprising the oxides and some oxide halides. The present investigation of the sulphates, selenates and chromates of mercury(II) was undertaken in order to find out whether such chains are also compatible with the presence of tetrahedral anions. This note will present a few results obtained during the preparative work and also some X-ray data.

In the literature, the existence of several sulphates, selenates and chromates of mercury(II) has been reported, *viz.*

Table 1. Observed and calculated values for the analyses and the densities. Calculated values are given within brackets.

Formulae	% Hg	% S	% Se	% Cr	% H_2O	Density $g \cdot cm^{-3}$
$HgSO_4$	67.3(67.6)	10.8(10.8)				6.49(6.50)
$HgSO_4 \cdot H_2O$	63.5(63.7)	10.2(10.2)			5.69(5.72)	5.44(5.45)
$Hg_3O_2SO_4$	82.3(82.5)	4.41(4.39)				8.32(8.43)
$HgSeO_4$	58.0(58.4)		24.0(23.0)			6.88(6.92)
$HgSeO_4 \cdot H_2O$	55.4(55.4)		22.4(21.8)		5.01(4.98)	5.60(5.61)
$Hg_3O_2SeO_4$	76.4(77.5)		10.9(10.2)			8.63(8.69)
$HgCrO_4$	63.3(63.4)			15.9(16.4)		6.06(6.10)
$HgCrO_4 \cdot (H_2O)_{\frac{1}{2}}$	61.3(61.6)			15.6(16.0)	2.76(2.76)	5.51(5.53)
$Hg_3O_2CrO_4$	79.9(80.2)			6.78(6.94)		8.39(8.46)

Table 2. Cell dimensions, cell volumes, cell contents, systematically absent spectra and probable space groups. The cell edges are given in Å, the cell volume in $Å^3$ and the cell content in formula units.

Formulae	*a*	*b*	*c*	β	V	Cell content	Systematically absent spectra (*n* is an integer)	Probable* space group
$HgSO_4$	4.817	6.577	4.783		151.5	2	$hk0{:}h+k=2n+1$	*Pmmn* (No. 59)
$HgSO_4 \cdot H_2O$	7.881	5.419	8.976		383.3	4	$0kl{:}k+l=2n+1$ $hk0{:}\ h=2n+1$	*Pnma* (No. 62)
$Hg_3O_2SO_4$	7.049		10.017		431.0	3	$00l{:}\ l \neq 3n$	$P3_121$ (No. 152)
$HgSeO_4$	4.979	6.721	4.928		164.9	2	$hk0{:}h+k=2n+1$	*Pmmn* (No. 59)
$HgSeO_4 \cdot H_2O$	7.769	7.712	8.249	120.0°	428.1	4	$h0l{:}l=2n+1$ $0k0{:}k=2n+1$	$P2_1/c$ (No. 14)
$Hg_3O_2SeO_4$	7.146		10.070		445.3	3	$00l{:}l \neq 3n$	$P3_1/21$ (No.152)
$HgCrO_4$	7.346	8.527	5.514	93.9°	344.5	4	$h0l{:}h+l=2n+1$ $0k0{:}k=2n+1$	$P2_1/n$ (No. 14)**
$HgCrO_4 \cdot (H_2O)_{\frac{1}{2}}$	11.837	5.526	14.638	120.9°	782.8	8	$hkl{:}h+k=2n+1$ $h0l{:}\ l=2n+1$	$C2/c$ (No. 15)
$Hg_3O_2CrO_4$	7.132		10.019		441.3	3	$00l{:}l \neq 3n$	$P3_121$ (No. 152)

* The probable space groups have been deduced from the Laue symmetry and the observed extinctions in the Weissenberg photographs. In the cases where the observed extinctions are characteristic of several space groups we have chosen the one with the highest symmetry as the probable one.

** Orientation different from that given in the *International Tables.*

$Hg_nO_{n-1}SO_4 \cdot mH_2O$ with $n = 1, m = 0; n = 1, m = 1; n = 3, m = 0;$
$n = \frac{3}{2}, m = 1$ (Refs.[1-3])

$Hg_nO_{n-1}SeO_4 \cdot mH_2O$ with $n = 1, m = 0; n = 1, m = 1; n = 3, m = \frac{1}{2}$ (Ref.[4])

$Hg_nO_{n-1}CrO_4 \cdot mH_2O$ with $n = 1, m = 0; n = 3, m = 0$ (Refs.[5-7])

Apart from the above compounds reported by other authors, we have found $Hg_3O_2SeO_4$ and $HgCrO_4(H_2O)_{\frac{1}{2}}$ which have not been reported before to our knowledge. On the other hand we have not yet been successful in preparing $Hg_3O(SO_4)_2(H_2O)_2$ reported by Hoitsema [1] and Paiĉ [3] and $Hg_3O_2SeO_4 \cdot (H_2O)_{\frac{1}{2}}$ reported by Cameron and Davy [4].

The substances $HgSO_4$, $HgSO_4 \cdot H_2O$, $HgSeO_4$, $HgSeO_4 \cdot H_2O$, $HgCrO_4$ and $HgCrO_4\ (H_2O)_{\frac{1}{2}}$ were synthesized by conventional methods starting from yellow HgO and H_2SO_4, H_2SeO_4 or CrO_3 and H_2O, respectively, while the oxide salts $Hg_3O_2SO_4$, $Hg_3O_2SeO_4$ and $Hg_3O_2CrO_4$ were obtained from $Hg(C_2H_3O_2)_2$ and the appropriate acid. By boiling yellow HgO with CrO_3 and H_2O, not only $HgCrO_4$ but also the new compound $HgCrO_4\ (H_2O)_{\frac{1}{2}}$ was prepared. $HgCrO_4\ (H_2O)_{\frac{1}{2}}$ looses its water of crystallization at about 200°C. An X-ray

Table 3. Part of the powder photographs of $HgSO_4$, $HgSeO_4$, $HgSO_4 \cdot H_2O$, $HgSeO_4 \cdot H_2O$, $HgCrO_4$, $HgCrO_4(H_2O)_{\frac{1}{2}}$, $Hg_3O_2SO_4$, $Hg_3O_2SeO_4$ and $Hg_3O_2CrO_4$. Guinier focusing camera of 80 mm diameter with $CuK\alpha_1$ radiation and potassium chloride as internal standard (a (KCl) = 6.2930 Å).

$HgSO_4$			
h k l	$10^4 \sin^2\Theta$ obs	$10^4 \sin^2\Theta$ calc	*I* obs
0 0 1	0260	0261	m
1 1 0	0394	0395	st
0 1 1	0398	0399	st
1 0 1	0518	0518	vst
0 2 0	0550	0552	vst
1 1 1	0655	0656	st
0 2 1	0812	0813	vw
2 0 0	1028	1028	m
0 0 2	1043	1042	w
1 2 1	1070	1070	st
0 1 2	1181	1180	m
2 0 1	1289	1289	vw
1 0 2	1300	1299	w
2 1 1 *	1426	1427	st
1 1 2 *	1438	1437	vw
1 3 0 0 3 1 }	1500	1499 1503 }	m
0 2 2	1594	1594	vw
1 3 1 *	1757	1760	m
1 2 2 *	1852	1851	m
2 0 2 *	2069	2070	w
0 4 0 2 1 2 }	2210	2208 2208 }	st

$HgSeO_4$			
h k l	$10^4 \sin^2\Theta$ obs	$10^4 \sin^2\Theta$ calc	*I* obs
0 0 1	0244	0246	m
1 1 0	0371	0373	st
0 1 1	0378	0378	m
1 0 1	0487	0486	vst
0 2 0	0528	0528	vst
1 1 1	0618	0618	vst
0 2 1	0772	0774	w
2 0 0	0961	0962	st
0 0 2	0982	0982	m
1 2 1	1014	1014	vst
0 1 2	1115	1114	vst
1 0 2	1223	1223	m
2 1 1	1338	1340	m
1 3 0 0 3 1 }	1431	1429 1434 }	m
2 2 0	1490	1490	st
0 2 2	1510	1510	vw
1 3 1 *	1675	1674	st
1 2 2	1750	1751	m
2 0 2	1944	1944	w
2 1 2 *	2075	2076	st
0 4 0	2110	2112	st
0 3 2	2169	2170	st

* By careful examination these lines were found to be faintly split.

powder photograph of a pure sample of $HgCrO_4(H_2O)_{\frac{1}{2}}$ which had been heated to 170°C for about 70 h gave only the lines of $HgCrO_4$ and showed the corresponding loss of weight. Upon studying commercial »mercuric chromates» from well-known manufacturers, it was found by chemical analyses and X-ray photography that some of them consisted of $HgCrO_4$ and others consisted of $Hg_3O_2CrO_4$.

The pure samples were analysed for Hg, S, Se, Cr and H_2O. The mercury analyses were made using electrolysis or by titrating Hg(II) with a standard solution of KSCN using Fe(III) as an indicator, and the sulphur analyses by precipitation of $BaSO_4$. The selenium analyses were performed by reducing the selenate ion to metallic selenium by adding a saturated solution of SO_2 to a strongly acid (HCl) solution of the salt. This method was, however, found to give slightly too high values. Chromium was determined titrimetrically by conventional methods with standard solutions of $Fe(NH_4)_2(SO_4)_2(H_2O)_6$ and

$HgSO_4 \cdot H_2O$			
h k l	$10^4\sin^2\Theta$ obs	$10^4\sin^2\Theta$ calc	*I* obs
1 0 1	0171	0170	m
0 1 1	0278	0277	st
0 0 2	0297	0296	m
1 1 1	0374	0373	m
1 0 2	0393	0392	w
2 0 1	0458	0458	st
2 1 0	0587	0587	st
2 1 1	0661	0661	vw
1 0 3	0763	0762	st
0 2 0	0813	0812	m
0 1 3	0870	0869	m
2 1 2	0881	0883	st
3 0 1	0937	0938	vw
1 1 3	0966	0965	m
1 2 1	0981	0982	m
2 0 3	1051	1050	m
0 2 2	1107	1108	m
3 0 2	1161	1160	vw
0 0 4	1184	1184	w
2 2 1	1268	1270	st
1 0 4	1280	1280	w
3 1 2	1363	1363	m
1 1 4	1484	1483	m
4 0 0	1535	1536	m
1 2 3	1573	1574	m
3 1 3	1735	1733	m
2 1 4	1772	1771	w
4 0 2	1833	1832	m
2 2 3	1861	1862	m

$HgSeO_4 \cdot H_2O$			
h k l	$10^4\sin^2\Theta$ obs	$10^4\sin^2\Theta$ calc	*I* obs
1 0 0	0131	0132	m
0 1 1	0216	0217	m
1 1 0	0232	0232	st
1 0 $\bar{2}$	0350	0351	w
0 2 0	0400	0401	st
1 1 $\bar{2}$	0451	0451	vst
0 0 2	0465	0467	w
1 1 1	0472	0473	vw
2 1 $\bar{1}$ 2 0 $\bar{2}$	0497	0496 0498	m
1 1 $\bar{1}$ 2 0 0	0527	0526 0527	vst
1 2 0	0533	0533	vw
0 1 2	0565	0568	vw
2 1 0	0628	0627	m
1 2 $\bar{2}$	0750	0752	m
1 2 1	0772	0774	m
2 2 $\bar{1}$	0796	0797	m
1 0 2	0846	0847	vw
0 2 2	0867	0868	st
2 2 $\bar{2}$	0899	0899	st
3 0 $\bar{2}$ 1 1 $\bar{3}$	0911	0909 0911	w
2 2 0	0929	0928	m
1 1 2	0948	0947	st
3 1 $\bar{2}$	1010	1009	m
3 1 $\bar{1}$ 1 3 0	1034	1031 1034	st
0 1 3	1148	1152	vw
1 2 2 1 3 $\bar{2}$	1251	1248 1253	m
1 3 1	1272	1275	w
3 1 0	1287	1286	w
3 2 $\bar{2}$	1311	1310	m
3 2 $\bar{1}$	1335	1332	m
2 3 $\bar{2}$ 2 0 $\bar{4}$	1403	1400 1404	m
2 3 0	1429	1429	w
0 2 3	1448	1452	w
2 1 $\bar{4}$ 1 0 $\bar{4}$	1501	1504 1505	m
3 2 3	1525	1522	vw
3 0 $\bar{4}$	1567	1567	w
2 1 2	1591	1590	st
0 4 0 1 1 $\bar{4}$	1602	1604 1605	m

$HgCrO_4$			
h k l	$10^4 \sin^2 \Theta$ obs	$10^4 \sin^2 \Theta$ calc	*I* obs
1 1 0	0192	0193	vst
1 0 $\bar{1}$	0288	0288	st
0 2 0 }	0328	0328 }	st
1 0 1 }		0328 }	
1 1 1	0369	0370	vw
2 0 0	0443	0444	st
0 2 1 }	0525	0525 }	vst
2 1 0 }		0526 }	
1 2 $\bar{1}$	0616	0616	vst
1 2 1	0657	0656	vst
2 0 1 }	0683	0681 }	vst
2 1 $\bar{1}$ }		0683 }	
2 1 1	0765	0763	vst
0 0 2	0790	0788	st
1 3 0	0848	0849	m
1 0 $\bar{2}$	0861	0859	vw
0 1 2	0871	0870	w
2 2 $\bar{1}$	0928	0929	w
1 0 2 }	0941	0939 }	w
1 1 $\bar{2}$ }		0941 }	
1 3 $\bar{1}$ }	1023	1026 }	w
1 1 2 }		1021 }	
1 3 1	1064	1066	w
3 1 0	1080	1081	st
0 2 2	1118	1116	m
2 0 $\bar{2}$	1151	1152	vw
2 3 0	1180	1182	w
2 1 2	1233	1234	w
1 2 2	1270	1267	w
2 0 2	1312	1312	w
3 1 1 }	1337	1336 }	w
3 2 0 }		1339 }	
2 1 2	1396	1394	vw
2 3 1 }	1422	1419 }	m
1 4 0 }		1423 }	
2 2 2	1478	1480	vw
0 4 1	1508	1508	m

$HgCrO_4(H_2O)_{\frac{1}{2}}$			
h k l	$10^4 \sin^2 \Theta$ obs	$10^4 \sin^2 \Theta$ calc	*I* obs
0 0 2	0149	0151	vw
2 0 0	0229	0231	m
1 1 0	0271	0273	st
1 1 $\bar{2}$	0325	0328	w
1 1 1	0357	0359	w
2 0 4	0448	0450	m
1 1 $\bar{3}$	0466	0468	vw
1 1 2	0518	0520	vw
2 0 2	0575	0574	vw
3 1 1	0626	0629	vw
1 1 $\bar{4}$	0683	0684	vst
4 0 2	0689	0692	vw
3 1 0	0735	0735	vst
4 0 $\bar{4}$ }	0760	0760 }	vst
3 1 $\bar{4}$ }		0762 }	
0 2 0	0860	0860	m
4 0 0	0926	0925	m
3 1 5	0954	0956	vw
1 1 $\bar{5}$	0975	0975	vw
2 2 1	1029	1032	vvw
1 1 4	1071	1068	m
2 2 0	1090	1091	m
2 2 $\bar{3}$	1142	1143	vw
2 2 1 }	1225	1225 }	w
3 1 6 }		1228 }	
5 1 $\bar{4}$	1303	1303	m
2 2 $\bar{4}$	1310	1310	w
1 1 $\bar{6}$	1346	1342	vvw
5 1 $\bar{5}$	1399	1403	vvw
0 2 4	1468	1465	m
6 0 4	1531	1532	w
4 2 $\bar{3}$ }	1552	1548 }	w
4 2 $\bar{2}$ }		1552 }	
2 2 $\bar{5}$ }		1554 }	
4 2 $\bar{4}$	1620	1620	m

$KMnO_4$. The water analyses were made according to Penfield[8]. The results of the analyses are in good agreement with the values calculated for the formulae of the compounds given (Table 1).

The densities of the substances were determined from the loss of weight in benzene. From Table 1 it is seen that the agreement between observed and calculated values is very good.

$Hg_3O_2SO_4$			
h k l	$10^4\sin^2\Theta$ obs	$10^4\sin^2\Theta$ calc	*I* obs
1 0 0	0158	0160	m
1 0 1	0218	0219	st
1 0 2	0396	0398	w
1 1 0	0479	0480	vw
0 0 3	0535	0535	vst
2 0 0	0639	0640	m
2 0 1	0700	0699	vst
1 1 2	0717	0718	m
2 0 2	0878	0879	vst
1 1 3	1015	1015	w
1 0 4	1110	1111	st
1 2 0	1121	1120	st
1 2 1	1179	1179	m
1 2 2	1358	1358	m
3 0 1	1502	1499	m
2 0 4	1593	1591	vst
3 0 2	1679	1678	m
2 2 0	1922	1920	st
1 1 5	1966	1966	m
2 2 1	1979	1981	m
1 3 0	2080	2079	m
2 0 5	2127	2126	st
1 3 1 } 0 0 6 }	2140	2139 } 2139 }	m
2 2 2	2160	2158	m

$Hg_3O_2SeO_4$			
h k l	$10^4\sin^2\Theta$ obs	$10^4\sin^2\Theta$ calc	*I* obs
1 0 0	0155	0156	m
1 0 1	0213	0214	m
1 0 2	0389	0391	vw
0 0 3	0529	0529	vst
2 0 0	0622	0622	m
2 0 1	0682	0681	vst
1 1 2	0702	0702	m
2 0 2	0857	0857	vst
1 1 3	0995	0996	vw
1 0 4	1096	1096	st
1 2 1 } 2 0 3 }	1150	1148 } 1151 }	m
1 2 2	1325	1324	vw
1 1 4	1407	1407	vw
3 0 1	1460	1459	vw
2 0 4	1565	1562	vw
1 0 5	1623	1625	st
3 0 2	1636	1635	st
2 2 0	1870	1867	m
1 1 5	1934	1936	m
1 2 4	2032	2029	vw
2 0 5	2094	2091	st
2 2 2	2105	2102	m
0 0 6	2118	2116	w
1 0 6	2274	2272	w

All of the compounds synthesized in this work were characterized by X-ray (powder and single crystal) methods. The cell dimensions, cell volumes, cell contents, systematically absent spectra and probable space groups are given in Table 2. Part of the powder patterns are given in Table 3.

The compounds $HgSO_4$ and $HgSeO_4$ were found to be isomorphous, likewise the compounds $Hg_3O_2SO_4$, $Hg_3O_2SeO_4$ and $Hg_3O_2CrO_4$. For $HgSO_4$, the same cell edges within the limits of experimental error have been recently reported by Kokkoros and Rentzeperis [9]. A faint splitting of some of the lines *hkl* and *h0l* in the X-ray powder photographs taken in a Guinier focusing camera may, however, indicate a lower symmetry. For $HgSO_4 \cdot H_2O$, the same cell edges and symmetry were found as those recently reported by Bonifačić[10].

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$Hg_3O_2CrO_4$			
h k l	$10^4 \sin^2\Theta$ obs	$10^4 \sin^2\Theta$ calc	*I* obs
1 0 0	0156	0156	m
1 0 1	0215	0215	st
1 0 2	0393	0394	vw
1 1 0	0469	0469	vw
0 0 3	0534	0535	vst
2 0 0	0625	0625	w
2 0 1	0686	0685	vst
1 0 3	0690	0691	m
1 1 2	0706	0707	m
2 0 2	0863	0863	vst
1 1 3	1004	1004	vw
1 2 0	1095	1094	m
1 0 4	1106	1106	m
1 2 1	1154	1153	w
2 0 3	1161	1160	w
1 2 2	1331	1332	vw
1 1 4	1419	1419	vw
3 0 1	1466	1466	vw
2 0 4	1576	1575	vst
1 2 3	1628	1629	m
1 0 5 } 3 0 2 }	1643	1641 } 1645 }	w
2 2 0	1876	1876	m
2 2 1	1934	1935	m
1 1 5	1954	1954	m
1 3 0	2032	2032	vw
1 2 4	2045	2044	w
1 3 1	2091	2091	w
2 0 5 } 2 2 2 }	2112	2110 } 2114 }	st
0 0 6	2137	2138	w

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