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The Crystal Structures of Some Mixed Halides of Lead

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The crystal structures of PbClBr, PbClI and PbBrI, determined from Weissenberg data, have been found to be isostructural with $PbCl_2$. For each structure the space group is *Pnam* and $Z=4$. The lattice parameters are $a=7{\cdot}80_4$, $b=9{\cdot}20_9$, $c=4{\cdot}578$ Å (PbClBr); $a=8{\cdot}818_8$, $b=9{\cdot}64_5$, $c=4{\cdot}595$ Å (PbClI);$a=8{\cdot}67_4$, $b=10{\cdot}48_3$, $c=4{\cdot}448$ Å (PbBrI).

Introduction

The crystal structure of $PbCl_2$ was determined by Braekken (1932) and partly refined by Sahl & Zemann (1961). The structure is orthorhombic with 4 molecules per unit cell, each atom being situated at the equipoint 4(*c*) of the space group *Pnam*. $PbBr_2$, α-PbF_2, Pb(OH)Cl and Pb(OH)Br are known to be isostructural with $PbCl_2$ (Wyckoff, 1963).

Specimens of PbClBr, PbClI and PbBrI have recently been synthesized in this department for infrared phosphorescent study. Each material was prepared by heating to melting point a mixture, consisting of 50% by molecular weight of the two appropriate lead dihalides, in a sealed evacuated silica tube and allowing the sample to cool slowly for several days. In each case single crystals were formed which were suitable for X-ray analysis by the Weissenberg technique.

X-ray powder data for these materials were obtained with crystal monochromatized Cu *Kα* radiation using a focusing camera of 22·9 cm effective diameter. The powder pattern is very similar to that of $PbCl_2$, and each can be indexed on the basis of an orthorhombic cell with parameters close to those of $PbCl_2$. This evidence suggested that $PbCl_2$ and the mixed halides of lead are isomorphous, and structure analyses of the latter have been carried out on this initial assumption. Lattice parameters calculated from powder data are compared with those of $PbCl_2$ in Table 1.

Table 1. *Lattice parameters*

Material	*a*	*b*	*c*
$PbCl_2$*	7·62 Å	9·05 Å	4·535 Å
PbClBr	$7{\cdot}80_4$	$9{\cdot}20_9$	4·578
PbClI	$8{\cdot}18_8$	$9{\cdot}64_5$	4·595
PbBrI	$8{\cdot}67_4$	$10{\cdot}48_3$	4·448

* Based on diffractometer data given by Swanson & Fuyat (1953).

The crystals used in the analyses were elongated parallel to the *c* axis. Consequently, intensity data were obtained from *c* axis equi-inclination Weissenberg photographs taken with Cu *Kα* radiation. The data appropriate to each crystal were as follows:

	PbClBr	PbClI	PbBrI
Mean radius (mm)	0·032	0·048	0·025
μr	3·9	7·8	3·7
Macroscopic density (g.cm^{-3})	6·40	—	—
X-ray density (g.cm^{-3})	6·51	6·76	6·80
No. of observed reflexions	253	273	282
No. of possible reflexions	277	289	307

No attempt was made to measure the densities of PbClI and PbBrI as it was known that the bulk material contained significant amounts of PbI_2.

For each analysis the intensities of reflexions on 3 layer lines were measured from multiple film exposures using a Joyce–Loebl flying spot microdensitometer; the intensities of weak reflexions had to be estimated visually against a calibrated scale. The systematically absent reflexions were such that $k+l=2n$ for $0kl$ and $h=2n$ for $h0l$, consistent with the space group *Pnam* (a non-standard setting of *Pnma*).

The observed reflexions were corrected for the Lorentz–polarization factor and for spot shape on upper layer lines (Phillips, 1954). Absorption corrections given by Bond (1959) were also applied assuming that each crystal was approximately of cylindrical shape.

The determination of the structure

The atomic scattering factors used to calculate structure factors were those given in *International Tables for X-ray Crystallography* (1962) for Cl^-, Br^- and neutral Pb and I.

Initially atoms were located at equipoint 4(*c*) of the space group *Pnam* at positions suggested by the $PbCl_2$ structure. These preliminary structures were refined by a three-dimensional least-squares program (Daly, Stephens & Wheatley, 1963) run on an Elliott 803 computer. After a few cycles of refinement, the atomic shifts became significantly less than the standard deviations. The final *R* values were 12·9% (PbClBr), 11·5% (PbClI) and 11·6% (PbBrI).

The final atomic parameters are listed in Table 2 together with those of $PbCl_2$ given by Sahl & Zemann (1961). Observed and calculated structure factors are compared in Table 3; in each analysis approximately half a dozen reflexions were found to be affected by extinction, and the observed values for these have been obtained from powder data.

Discussion of the structure

The crystal structure of PbXY, where X and Y represent the lighter and heavier halogen ions, respectively, is shown diagrammatically in Fig. 1 which has been drawn from the data for PbClI. The positions of the halogen ions in the mixed halides, particularly PbClBr and PbClI, are very similar to those of chlorine in $PbCl_2$. There is, however, a prominent shift in the location of the lead ion as one progresses from the structure of $PbCl_2$ at one end of the series to that of PbBrI at the other. This shift is such as to increase the Pb–Y separation in the *xy*-plane; for instance in $PbCl_2$ the separation (2·86 Å) is of the same order of magnitude as the sum of the ionic radii, whereas in PbBrI it is so great (4·53 Å) that the ions can hardly be thought of as being adjacent.

Table 2. *Atomic parameters* (*origin at* $\bar{1}$)
Standard deviations are given in parentheses.

	x	y	z	B (Å^2)
Pb	0·2617	0·0956	¼	2·0
Cl	0·8610	0·0742	¼	2·0
Cl$^{\mathrm{I}}$	0·4768	0·8370	¼	2·0
Pb	0·2462 (3)	0·1040 (3)	¼	4·47 (06)
Cl	0·8584 (14)	0·0675 (12)	¼	3·30 (21)
Br	0·4732 (7)	0·8322 (5)	¼	3·44 (09)
Pb	0·2078 (3)	0·1251 (2)	¼	4·29 (05)
Cl	0·8600 (12)	0·0620 (10)	¼	2·18 (17)
I	0·4707 (3)	0·8307 (3)	¼	2·31 (05)
Pb	0·1624 (2)	0·1578 (2)	¼	3·33 (05)
Br	0·8412 (3)	0·0542 (4)	¼	1·80 (07)
I	0·5007 (3)	0·8288 (2)	¼	2·42 (06)

Each lead ion is surrounded by 2X and 1Y in the same *xy*-plane and 1X and 2Y lying in each adjacent plane. The nearest halogens to X are 2Y in the same *xy*-plane and 1X and 2Y in the neighbouring planes. Each Y ion has a halogen coordination of ten, 2X and 2Y in the same *xy*-plane and 2X and 1Y in each neighbouring plane. Bond lengths for $PbCl_2$ and the mixed halides are given in Table 4. It will be seen that there is a wide range of bond lengths between any particular

Table 3. *Observed and calculated structure factors for* (*a*) PbClBr, (*b*) PbClI *and* (*c*) PbBrI

Reflexions too weak to be observed are allocated an intensity $I_0 = I_{\min}/2$, where $I_{\min}$ is the smallest intensity on the scale used for visual estimates. Observed structures factors for the following reflexions were obtained from powder data: (*a*) 020, 120, 130, 400, 111, 122, 132, 142; (*b*) 400, 310, 401, 211, 312; (*c*) 020, 250, 310, 031.

(*a*)

H	K	L	F_c	F_o
0	2	0	53	47
0	4	0	-235	228
0	6	0	-61	70
0	8	0	4	5
0	10	0	31	26
1	2	0	-219	207
1	3	0	109	112
1	4	0	- 90	118
1	5	0	-54	73
1	6	0	110	129
1	7	0	-36	38
1	8	0	78	77
1	9	0	26	23
1	10	0	-22	19
1	11	0	-10	8
2	0	0	-178	146
2	1	0	-19	30
2	2	0	-124	103
2	3	0	29	37
2	4	0	130	109
2	5	0	44	41
2	6	0	152	156
2	7	0	-6	5
2	8	0	-55	61
2	9	0	-6	6
2	10	0	-51	39
3	1	0	-90	91
3	2	0	257	236
3	3	0	68	65
3	4	0	67	65
3	5	0	-7	5
3	6	0	-74	84
3	7	0	-1	5
3	8	0	-49	53
3	9	0	28	24
3	10	0	-3	5
4	0	0	221	214
4	1	0	-37	39
4	2	0	-3	4
4	3	0	5	5
4	4	0	-139	138
4	5	0	20	10
4	6	0	-21	27
4	7	0	-29	33
4	8	0	27	30
4	9	0	2	[illegible]
4	10	0	30	21
5	1	0	-13	18
5	2	0	-110	123
5	3	0	30	23
5	4	0	-108	98
5	5	0	-25	21
5	6	0	47	50
5	7	0	-7	7
5	8	0	61	55
5	9	0	19	21
5	10	0	-11	12
6	0	0	-72	75
6	1	0	-53	53
6	2	0	-33	28
6	3	0	-26	20
6	4	0	61	50
6	5	0	17	21
6	6	0	53	44
6	7	0	-13	13
6	8	0	-30	22
7	1	0	-4	5
7	2	0	101	90
7	3	0	22	23
7	4	0	5	7
7	5	0	-2	4
7	6	0	-30	26
7	7	0	-11	17
8	0	0	71	82
8	1	0	-14	17
8	2	0	16	22
8	3	0	17	17
8	4	0	-41	41
8	5	0	22	18
8	6	0	-23	35
9	1	0	5	3
9	2	0	-11	17
9	3	0	-2	8
9	4	0	-23	32
10	0	0	-32	33
10	1	0	-15	12
0	3	1	-258	256
0	5	1	-65	74
0	7	1	145	125
0	9	1	30	26
0	11	1	-32	28
1	1	1	-186	182
1	2	1	-119	·113
1	3	1	110	113
1	4	1	47	53
1	5	1	143	158
1	6	1	-8	8
1	7	1	-3	8
1	8	1	-27	24
1	9	1	-58	54
1	10	1	26	21
1	11	1	-22	[illegible]
2	0	1	70	73
2	1	1	237	222
2	2	1	8	5
2	3	1	195	203
2	4	1	-8	5
2	5	1	-65	76
2	6	1	5	5
2	7	1	-57	71
2	8	1	-22	25
2	9	1	-26	26
2	10	1	[illegible]	5
2	11	1	[illegible]	7
3	1	1	160	148
3	2	1	-25	25
3	3	1	-26	30
3	4	1	81	91
3	5	1	-150	160
3	6	1	2	5
3	7	1	-28	28
3	8	1	-31	28
3	9	1	55	52
3	10	1	9	14
3	11	1	12	9
4	0	1	52	51
4	1	1	-43	43
4	2	1	-26	39
4	3	1	-114	114
4	4	1	-27	32
4	5	1	-4	5
4	6	1	26	39
4	7	1	98	91
4	8	1	-2	4
4	9	1	10	16
5	1	1	-149	149
5	2	1	-43	38
5	3	1	77	72
5	4	1	26	36
5	5	1	79	79
5	6	1	7	17
5	7	1	10	21
5	8	1	-9	16
5	9	1	-12	20
6	0	1	10	12
6	1	1	80	86
6	2	1	-33	36
6	3	1	72	51
6	4	1	-4	5
6	5	1	-30	39
6	6	1	38	40
6	7	1	-35	34
6	8	1	-5	14
6	9	1	-9	12
7	1	1	42	53
7	2	1	-10	17
7	3	1	5	6
7	4	1	3	10
7	5	1	-62	57
7	6	1	-11	21
7	7	1	-12	20
8	0	1	46	56
8	1	1	-30	40
8	2	1	-5	9
8	3	1	-49	54
8	4	1	-18	27
8	5	1	-4	7
8	6	1	7	14
9	1	1	-30	38
9	2	1	-7	6
9	3	1	31	34
0	2	2	-33	52
0	4	2	170	156
0	6	2	44	58
0	8	2	-2	5
0	10	2	-23	23
1	2	2	154	150
1	3	2	-77	74
1	4	2	66	55
1	5	2	41	54
1	6	2	-82	·97
1	7	2	28	26
1	8	2	-59	59
1	9	2	-21	17
1	10	2	17	19
1	11	2	8	7
2	0	2	122	110
2	1	2	15	15
2	2	2	87	110
2	3	2	-19	42
2	4	2	-94	118
2	5	2	-33	42
2	6	2	-116	120
2	7	2	5	7
2	8	2	43	46
2	9	2	5	6
2	10	2	40	28
3	1	2	63	64
3	2	2	-186	204
3	3	2	-51	66
3	4	2	-48	64
3	5	2	6	5
3	6	2	55	60
3	7	2	1	5
3	8	2	37	41
3	9	2	-23	26
3	10	2	3	2
4	0	2	-164	132
4	1	2	28	29
4	2	2	3	5
4	3	2	-3	3
4	4	2	105	106
4	5	2	-15	10
4	6	2	14	24
4	7	2	23	31
4	8	2	-21	30
4	9	2	-1	6
4	10	2	-23	14
5	1	2	10	10
5	2	2	82	75
5	3	2	-23	27
5	4	2	83	79
5	5	2	19	25
5	6	2	-36	41
5	7	2	6	4
5	8	2	-48	37
5	9	2	-15	10
6	0	2	53	65
6	1	2	42	49
6	2	2	25	32
6	3	2	20	26
6	4	2	-46	46
6	5	2	-13	14
6	6	2	-41	36
6	7	2	11	19
6	8	2	23	18
7	1	2	3	4
7	2	2	-78	84
7	3	2	-17	27
7	4	2	-3	4
7	5	2	2	3
7	6	2	23	25
7	7	2	9	13
8	0	2	-55	69
8	1	2	11	17
8	2	2	-12	17
8	3	2	-14	19
8	4	2	32	42
8	5	2	-17	14
8	6	2	18	19
9	1	2	-4	2
9	2	2	8	12
9	3	2	2	5

Table 3 (*cont.*)

(*b*)

H	K	L	F_c	F_o
0	2	0	−58	87
0	4	0	−294	292
0	6	0	97	92
0	8	0	28	20
0	10	0	−33	33
1	2	0	−213	235
1	3	0	131	165
1	4	0	9	9
1	5	0	−117	116
1	6	0	169	152
1	7	0	−30	29
1	8	0	12	20
1	9	0	73	72
1	10	0	−76	72
1	11	0	−44	46
2	0	0	−82	91
2	1	0	−135	126
2	2	0	−91	111
2	3	0	−39	39
2	4	0	118	115
2	5	0	130	122
2	6	0	105	110
2	7	0	20	23
2	8	0	−124	121
2	9	0	−29	30
2	10	0	−16	19
2	11	0	−13	10
3	1	0	−223	248
3	2	0	239	223
3	3	0	211	205
3	4	0	−45	44
3	5	0	31	30
3	6	0	−76	81
3	7	0	−66	71
3	8	0	32	31
3	9	0	34	42
3	10	0	4	6
3	11	0	−1	4
4	0	0	166	160
4	1	0	36	32
4	2	0	−75	62
4	3	0	99	98
4	4	0	−112	116
4	5	0	−34	37
4	6	0	82	76
4	7	0	−119	108
4	8	0	21	19
4	9	0	44	47
4	10	0	−3	4
5	1	0	65	52
5	2	0	21	19
5	3	0	−34	37
5	4	0	−94	109
5	5	0	−102	116
5	6	0	14	21
5	7	0	41	47
5	8	0	37	49
5	9	0	68	55
5	10	0	−34	20
6	0	0	60	50
6	1	0	−172	130
6	2	0	−13	21
6	3	0	−90	86
6	4	0	−18	18
6	5	0	101	134
6	6	0	24	35
6	7	0	−12	14
6	8	0	−21	18
6	9	0	−17	19
7	1	0	−55	48
7	2	0	36	36
7	3	0	34	80
7	4	0	−62	57
7	5	0	28	35
7	6	0	20	23
7	7	0	−50	51
7	8	0	34	27
8	0	0	−17	21
8	1	0	−11	12
8	2	0	5	6
8	3	0	50	51
8	4	0	26	31
8	5	0	22	26
8	6	0	−2	4
8	7	0	−57	35
9	1	0	25	29
9	2	0	87	98
9	3	0	−25	26
9	4	0	−29	31
9	5	0	−14	14
10	0	0	9	16
10	1	0	−44	30
0	3	1	−219	272
0	5	1	−9	9
0	7	1	163	162
0	9	1	−57	55
0	11	1	−54	71
1	2	1	−232	252
1	3	1	200	218
1	4	1	100	107
1	5	1	95	98
1	6	1	14	22
1	7	1	−104	94
1	8	1	−63	66
1	9	1	−50	53
1	10	1	44	50
1	11	1	19	10
2	1	1	292	281
2	2	1	2	7
2	3	1	130	134
2	4	1	74	74
2	5	1	−165	157
2	6	1	19	18
2	7	1	12	17
2	8	1	−81	85
2	9	1	32	30
2	10	1	67	74
2	11	1	−10	9
3	1	1	68	82
3	2	1	68	55
3	3	1	−16	19
3	4	1	120	126
3	5	1	−108	122
3	6	1	−79	82
3	7	1	22	19
3	8	1	−47	48
3	9	1	55	63
3	10	1	67	74
3	11	1	−35	25
4	0	1	238	203
4	1	1	33	28
4	2	1	−53	54
4	3	1	−33	41
4	4	1	−156	162
4	5	1	4	7
4	6	1	64	74
4	7	1	88	98
4	8	1	39	42
4	9	1	−30	26
4	10	1	−8	9
4	11	1	−42	23
5	1	1	−92	79
5	2	1	−186	155
5	3	1	93	85
5	4	1	59	63
5	5	1	−14	6
5	6	1	83	111
5	7	1	−17	14
5	8	1	−28	32
5	9	1	43	47
5	10	1	−12	3
6	0	1	−52	44
6	1	1	30	24
6	2	1	−56	51
6	3	1	−14	15
6	4	1	60	63
6	5	1	−35	33
6	6	1	68	78
6	7	1	21	19
6	8	1	−62	66
6	9	1	−1	7
7	1	1	−56	45
7	2	1	49	47
7	3	1	83	86
7	4	1	−1	5
7	5	1	−20	[illegible]
7	6	1	−33	56
7	7	1	−26	36
7	8	1	[illegible]	8
8	0	1	130	140
8	1	1	24	28
8	2	1	−24	17
8	3	1	10	10
8	4	1	−68	67
8	5	1	−30	37
8	6	1	40	37
8	7	1	−11	7
9	1	1	12	20
9	2	1	−28	28
9	3	1	30	28
9	4	1	−2	3
9	5	1	−44	26
10	0	1	30	25
10	1	1	−26	24
10	2	1	−15	12
0	2	2	48	63
0	4	2	213	216
0	6	2	−79	85
0	8	2	−16	12
0	10	2	23	34
1	1	2	6	4
1	2	2	149	128
1	3	2	−101	99
1	4	2	−4	6
1	5	2	92	87
1	6	2	−120	121
1	7	2	26	23
1	8	2	−10	14
1	9	2	−60	68
1	10	2	60	66
1	11	2	37	27
2	0	2	48	47
2	1	2	98	71
2	2	2	69	71
2	3	2	29	25
2	4	2	−83	79
2	5	2	−100	95
2	6	2	−96	90
2	7	2	−14	14
2	8	2	98	99
2	9	2	22	26
2	10	2	13	20
2	11	2	10	6
3	1	2	164	167
3	2	2	[illegible]	71
3	3	2	−162	156
3	4	2	36	33
3	5	2	−28	21
3	6	2	57	64
3	7	2	51	61
3	8	2	−26	26
3	9	2	−31	42
3	10	2	−1	3
3	11	2	2	1
4	0	2	−129	[illegible]
4	1	2	−21	18
4	2	2	59	51
4	3	2	−73	75
4	4	2	86	100
4	5	2	22	27
4	6	2	−60	72
4	7	2	87	99
4	8	2	−15	14
4	9	2	−35	42
4	10	2	5	2
5	1	2	−46	39
5	2	2	−19	19
5	3	2	22	24
5	4	2	78	93
5	5	2	80	95
5	6	2	−10	12
5	7	2	−31	38
5	8	2	−32	45
5	9	2	−56	57
6	0	2	−50	39
6	1	2	137	111
6	2	2	11	17
6	3	2	70	77
6	4	2	15	17
6	5	2	−80	94
6	6	2	−20	31
6	7	2	13	13
6	8	2	16	17
6	9	2	13	9
7	1	2	41	39
7	2	2	−32	32
7	3	2	−67	74
7	4	2	52	52
7	5	2	−20	25
7	6	2	−16	22
7	7	2	41	41
7	8	2	−29	20
8	0	2	12	12
8	1	2	12	12
8	2	2	−4	4
8	3	2	−40	45
8	4	2	−20	26
8	5	2	−21	25
8	6	2	2	2
9	1	2	−19	23
9	2	2	−72	90
9	3	2	20	14
9	4	2	24	21

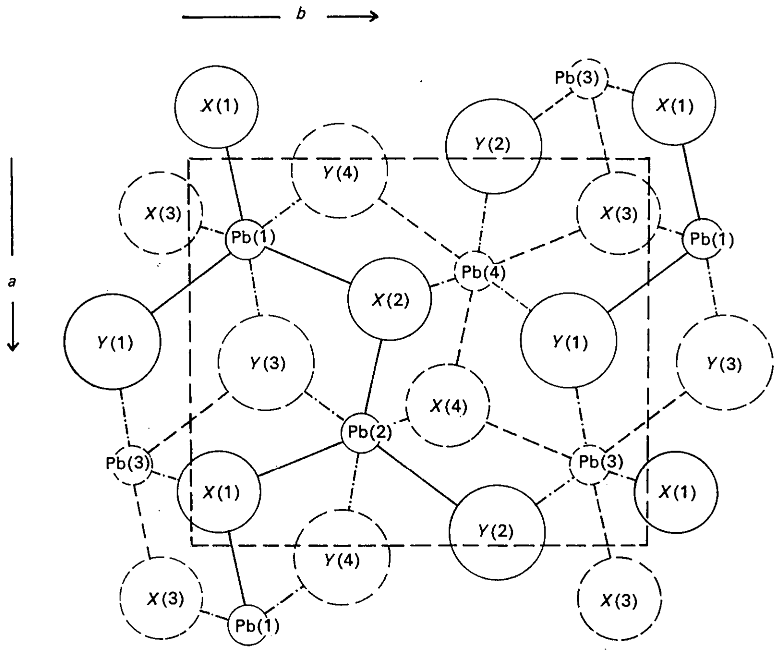

Fig. 1. Projection of the structure of PbXY on the (001) face of the unit cell. X and Y represent the lighter and heavier halogen atoms respectively. Atoms labelled (1) and (2) are at $z=\frac{1}{4}$ and those labelled (3) and (4) at $z=\frac{3}{4}$.

Table 3 (*cont.*)

(*c*)

H	K	L	F_c	F_o
0	2	0	-125	125
0	4	0	-203	213
0	6	0	261	224
0	8	0	-135	121
0	10	0	-145	124
0	12	0	69	62
1	2	0	-163	151
1	3	0	66	75
1	4	0	236	213
1	5	0	-65	66
1	6	0	113	103
1	7	0	3	2
1	8	0	-91	77
1	9	0	-5	6
1	10	0	26	24
1	11	0	-64	59
2	0	0	4	3
2	1	0	-174	155
2	2	0	-83	79
2	3	0	46	57
2	4	0	3	2
2	5	0	251	261
2	6	0	55	51
2	7	0	-36	33
2	8	0	-32	28
2	9	0	-41	33
2	10	0	39	30
2	11	0	40	37
2	12	0	31	26
3	1	0	-316	295
3	2	0	-10	6
3	3	0	316	283
3	4	0	27	35
3	5	0	-103	106
3	6	0	14	1[illegible]
3	7	0	-31	39
3	8	0	-7	6
3	9	0	205	182
3	10	0	2	1
3	11	0	-2	1
3	12	0	-2	1
4	0	0	-49	57
4	1	0	126	123
4	2	0	-73	85
4	3	0	-2[illegible]	3[illegible]
4	4	0	13	1[illegible]
4	5	0	-133	138
4	6	0	3[illegible]	3[illegible]
4	7	0	31	34
4	8	0	-13	30
4	9	0	31	28
4	10	0	52	50
4	11	0	-32	25
5	1	0	1	4
5	2	0	[illegible]	115
5	3	0	60	65
5	4	0	-170	131
5	5	0	-4[illegible]	56
5	6	0	-[illegible]0	108
5	7	0	-3	3
5	8	0	64	70
5	9	0	1[illegible]	25
5	10	0	-17	21
5	11	0	-41	3[illegible]
6	0	0	325	24[illegible]
6	1	0	16	19
6	2	0	-61	74
6	3	0	-13	19
6	4	0	-109	126
6	5	0	-37	37
6	6	0	146	163
6	7	0	1	[illegible]
6	8	0	-15	14
6	9	0	4	3
6	10	0	[illegible]	[illegible]1
7	1	0	47	51
7	2	0	-66	[illegible]
7	3	0	3[illegible]	31
7	4	0	[illegible]5	114
7	5	0	-33	3[illegible]
7	6	0	[illegible]	40
7	7	0	-3	2
7	8	0	-4[illegible]	42
8	0	0	34	44
8	1	0	-[illegible]	64
8	2	0	-31	31
8	3	0	27	30
8	4	0	-[illegible]	16
8	5	0	112	124
8	6	0	34	32
8	7	0	-[illegible]	6
8	8	0	-24	29
9	1	0	-104	112
9	2	0	-6	6
9	3	0	101	114
9	4	0	30	33
9	5	0	-30	44
9	6	0	17	23
10	0	0	-26	33
10	1	0	29	37
10	2	0	-32	34
10	3	0	-9	12
0	3	1	-147	142
0	5	1	4	15
0	7	1	-43	42
0	9	1	-74	61
1	2	1	-30[illegible]	282
1	3	1	251	245
1	4	1	167	160
1	5	1	-50	59
1	6	1	-23	27
1	7	1	-142	113
1	8	1	-142	118
1	9	1	32	23
1	10	1	[illegible]	73
1	11	1	-23	17
1	12	1	13	13
2	0	1	-134	145
2	1	1	261	233
2	2	1	164	167
2	3	1	39	45
2	4	1	144	144
2	5	1	-145	122
2	6	1	-170	139
2	7	1	150	124
2	8	1	-41	35
2	9	1	5	[illegible]
2	10	1	24	21
2	11	1	-74	66
2	12	1	-56	46
3	1	1	5	6
3	2	1	142	158
3	3	1	21	31
3	4	1	58	57
3	5	1	-4	6
3	6	1	-4	6
3	7	1	-15	16
3	8	1	75	68
3	9	1	-2	0
3	10	1	3	13
3	11	1	-4	6
4	0	1	96	96
4	1	1	234	221
4	2	1	-112	121
4	3	1	54	69
4	4	1	-103	114
4	5	1	-120	129
4	6	1	122	124
4	7	1	146	141
4	8	1	31	27
4	9	1	10	14
4	10	1	-19	14
4	11	1	-76	70
5	1	1	17	6
5	2	1	-164	180
5	3	1	-181	204
5	4	1	113	134
5	5	1	39	40
5	6	1	-14	16
5	7	1	112	114
5	8	1	-84	90
5	9	1	-20	21
5	10	1	60	62
6	0	1	0	3
6	1	1	-53	58
6	2	1	-23	16
6	3	1	-81	92
6	4	1	-16	19
6	5	1	-10	6
6	6	1	20	18
6	7	1	-23	20
6	8	1	12	13
6	9	1	-45	31
7	1	1	-11	6
7	2	1	-161	172
7	3	1	95	107
7	4	1	73	36
7	5	1	-20	18
7	6	1	-24	16
7	7	1	-61	69
7	8	1	-96	95
7	9	1	12	20
8	0	1	-41	53
8	1	1	85	90
8	2	1	73	83
8	3	1	4	6
8	4	1	61	71
8	5	1	-59	68
8	6	1	-78	84
8	7	1	57	62
9	1	1	9	6
9	2	1	41	43
9	3	1	22	22
9	4	1	34	27
10	0	1	15	21
10	1	1	31	32
10	2	1	-23	24
10	3	1	26	33
0	2	2	[illegible]	100
0	4	2	155	166
0	6	2	-202	192
0	8	2	111	95
0	10	2	119	34
1	1	2	-43	54
1	2	2	115	112
1	3	2	-52	5[illegible]
1	4	2	-179	166
1	5	2	52	54
1	6	2	-30	34
1	7	2	1	7
1	8	2	70	64
1	9	2	4	7
1	10	2	-20	23
1	11	2	54	4[illegible]
2	0	2	-5	7
2	1	2	124	122
2	2	2	63	74
2	3	2	-37	41
2	4	2	0	6
2	5	2	-1[illegible]6	16[illegible]
2	6	2	-47	47
2	7	2	26	21
2	8	2	26	25
2	9	2	33	2[illegible]
2	10	2	-32	27
2	11	2	-31	2[illegible]
3	1	2	23[illegible]	232
3	2	2	7	7
3	3	2	-240	242
3	4	2	-21	7
3	5	2	[illegible]	7
3	6	2	-11	7
3	7	2	6[illegible]	7[illegible]
3	8	2	5	7
3	9	2	-16[illegible]	164
3	10	2	-2	1
4	0	2	36	41
4	1	2	-[illegible]4	10[illegible]
4	2	2	5	[illegible]
4	3	2	25	3[illegible]
4	4	2	-[illegible]	6
4	5	2	146	156
4	6	2	-33	3[illegible]
4	7	2	-22	31
4	8	2	10	15
4	9	2	-25	19
5	1	2	-1	3
5	2	2	-74	[illegible]1
5	3	2	-50	65
5	4	2	136	159
5	5	2	40	44
5	6	2	74	92
5	7	2	4	7
5	8	2	-50	63
5	9	2	-260	246
6	1	2	-12	[illegible]
6	2	2	47	62
6	3	2	11	7
6	4	2	[illegible]6	105
6	5	2	30	3[illegible]
6	6	2	-117	142
6	7	2	[illegible]	1
6	8	2	72	77
7	1	2	-3[illegible]	45
7	2	2	46	59
7	3	2	-27	27
7	4	2	-73	[illegible]4
7	5	2	[illegible]	36
7	6	2	-40	43
7	7	2	5	7
7	8	2	32	33
8	0	2	-29	17
8	1	2	45	30
8	2	2	26	24
8	3	2	-23	23
8	4	2	[illegible]	6
8	5	2	-92	104
8	6	2	-30	35
9	1	2	37	33
9	2	2	5	4
9	3	2	-32	61
9	4	2	-25	22

Table 4. *Bond lengths*

Standard deviations are given in parentheses. Identification of atoms as in Fig. 1.

Bond		PbClBr	PbClI	PbBrI	$PbCl_2$
Pb(1)–X(1)		3·044 (10) Å	2·913 (8) Å	2·990 (4) Å	3·06 Å
–X(2)		3·151 (10)	3·265 (8)	3·393 (4)	3·08
–X(3)		2·898 (10) 2×	2·974 (8) 2×	3·145 (4) 2×	2·90 2×
–Y(1)		3·065 (5)	3·565 (3)	4·529 (3)	2·86
–Y(3)		3·223 (5) 2×	3·520 (3) 2×	3·675 (3) 2×	3·08 2×
–Y(4)		3·548 (5) 2×	3·367 (3) 2×	3·188 (3) 2×	3·64 2×
X(1)–X(3)		3·416 (14) 2×	3·459 (12) 2×	3·719 (5) 2×	3·38 2×
–Y(1)		3·706 (10)	3·890 (8)	3·783 (4)	3·63
X(1)–Y(2)	Y(1)–X(2)	3·788 (10)	3·894 (8)	4·247 (4)	3·82
–Y(3)	–X(3)	3·575 (10) 2×	3·699 (8) 2×	3·905 (4) 2×	3·52 2×
–Y(4)	–X(4)	3·594 (10) 2×	3·730 (8) 2×	3·887 (4) 2×	3·51 2×
Y(1)–Y(2)		4·186 (6) 2×	4·379 (3) 2×	4·641 (4) 2×	4·12 2×
–Y(3)		3·869 (6) 2×	4·022 (3) 2×	4·223 (4) 2×	3·74 2×

pair of ions, showing that the arrangement of the halogen ions departs considerably from a close-packed array. In each structure the shortest bond length between any two halogen ions is less than the sum of the ionic radii as given by Clark (1955).

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The Crystal Structure of Copper Mercury Oxynitrate Trihydrate, $Cu(NO_3)_2 . HgO . 3H_2O$

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The crystal structure of copper(II) mercury(II) oxynitrate trihydrate has been determined by single-crystal three-dimensional X-ray analysis. There are two formula units in the monoclinic unit cell of dimensions $a=7·33$, $b=8·87$, $c=6·75$ Å, $\beta=112°32'$ and space group $P2_1/c$. The copper ion is coordinated by two oxygen atoms from two nitrate ions at 2·14 Å, two oxygen atoms from two hydroxide ions at 2·15 Å and two oxygen atoms from two water molecules at 2·02 Å in an octahedron. Both hydroxide ions and both water molecules belong simultaneously to the mercury ion, at 2·30 and 2·54 Å respectively, whose octahedral coordination is completed with nitrate-oxygen atoms at 2·78 Å. The octahedra about copper and mercury are linked alternately by sharing two opposite edges along the *c* axis as well as two opposite corners along the *b* axis. The solution of the structure shows that the best definition of the chemical formula of this compound is $HgCu(OH)_2(NO_3)_2 . 2H_2O$.

Introduction

Among various basic salts there is a large group of those with the general formula $mMX_2 . nHgO . xH_2O$ where M = Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd, Hg, and X = Cl^-, Br^-, NO_3^-, SO_4^{2-}, SeO_4^{2-}, ClO_3^-, BrO_3^-. (André, 1887; Maihle, 1902; Finzi, 1913; Denk & Dewald, 1951; Denk, Leschhorn & Rosmer, 1962; Denk & Leschhorn, 1966). With the exception of mercury oxyhalides, basic mercuric sulphates, chlorate and bromate where M = Hg, the structures of other salts are still unknown (Grdenić, 1965).

We have undertaken the crystal-structure investigation of the basic nitrate $Cu(NO_3)_2 . HgO . 3H_2O$ in order to establish to which structural type it belongs (Basset, 1947). It was particularly interesting to find out the coordination about mercury in the presence of another metal. At the same time, in spite of many solved structures, the stereochemistry of copper still attracts attention. Not of less interest have been also the ligand properties of the nitrate ion, particularly since Wallwork & Addison (1965) proposed its bidentate character in the structure of anhydrous α-copper(II) nitrate.

Experimental

$(NO_3)_2Hg . CuO . 5H_2O$ is reported to have been obtained by dissolving mercuric oxide in an aqueous solution of cupric nitrate (Maihle, 1902). By the same method $Cu(NO_3)_2 . HgO . 3H_2O$ was prepared in the form of pale blue needle-shaped crystals ((Finzi, 1913). All our attempts to prepare both compounds have always resulted in the trihydrate.

The crystal data are as follows:

$a=7·33\pm0·02$ Å Formula weight 458·2
$b=8·87\pm0·02$ $V=405·3$ Å^3
$c=6·75\pm0·02$ $\varrho_m=3·74$ g.cm^{-3}
$\beta=112°32'\pm15'$ $\varrho_x=3·75$ g.cm^{-3}
Space group $P2_1/c$ $Z=2$

The cell parameters were measured from oscillation and Weissenberg photographs. Density was determined pycnometrically. The systematic absence of reflexions *h*0*l* for *l* odd and 0*k*0 for *k* odd uniquely determined the space group as $P2_1/c$. Except for some weak reflexions, all *hkl* reflexions fulfil the condition $k+l=2n$ required by the special positions of the heavy atoms. Three-dimensional intensity data (*h*0*l* … *h*6*l*, *hk*0 … *hk*6) were recorded on integrated equi-inclination Weissenberg photographs with multiple films with Cu *Kα* radiation and determined photometrically. Within the limiting sphere 526 independent reflexions were strong enough to be observed. After correction for Lorentz and polarization factors, the intensities were placed on the same