LEAD OXYACIDS AND HALIDE COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA

Clive E. Holloway[1] and Milan Melnik*[2]

[1] Department of Chemistry, York University, 4700 Keele St., North York, M3J1P3. Ontario, Canada
[2] Department of Inorganic Chemistry, Slovak Technical University, Radlinskeho 9, SL 81237, Bratislava, Slovak Republic

This review is the last of three reviews covering the structures of lead compounds, and covers over two hundred lead oxoacids and halides, only fourteen of which have the lead atom in its +4 oxidation state. Only octahedral coordination is found for Pb(IV), but the coordination around Pb(II) varies from trigonal to dodecahedral. Bond distances and interbond angles are correlated with covalent radii of the ligand atoms, and the effect of the non-bonded pair of valence electrons on Pb(II) is discussed. There are examples of distortion and structural isomerism in these derivatives.

CONTENTS

1. INTRODUCTION

Lead is one of the oldest known metals and by far the most abundant of the heavy metals. The most important lead ore is black galena (PbS), with other ore minerals being anglesite ($PbSO_4$), cerussite ($PbCO_3$), pyromorphite ($Pb_5(PO_4)_3Cl$) and mimetesite ($Pb_5(AsO_4)_3Cl$. Some twenty five other minerals are known [1], all containing Pb(II). Lead is still widely used, the major application being the familiar storage battery. Other uses include organolead compounds ($PbMe_4$ and $PbEt_4$) as fuel octane enhancers and inorganic lead compounds as pigments. Lead has long been recognised as a heavy metal poison which inhibits many biological enzymes. These factors have stimulated a continuing interest in lead chemistry, including nearly one thousand structural studies. The coordination, inorganic and heterometallic derivatives have been reviewed previously [2,3], and an often complicated stereochemistry is observed for the Pb(II) derivatives because of the non-bonded pair of valence electrons. This survey looks at the more than two hundred lead oxoacids and halide derivatives of lead for which structural data is available.

2. LEAD INORGANIC SALTS

The structural data for lead inorganic salts are gathered in Table 1. These are listed and referenced in order of their anions: hydroxides, pseudohalogens, and derivatives of oxoacids (MO_x, where M is a non-metal or metalloid).

Lead does not appear to form a simple hydroxide, $Pb(OH)_2$, but instead forms hydrolysis and condensation products as the pH of a Pb(II) salt solution is raised. Thus dissolution of PbO in aqueous $HClO_4$, followed by careful neutralisation, leads to $[Pb_6O(OH)_6](ClO_4)_4.H_2O$. This cluster cation of lead [4] consists of three tetrahedra of lead sharing faces. The central tetrahedron encompasses the unique O(1) atom, and the six hydroxy groups lie on the faces of the second tetrahedra, as shown in Figure 1. The extent of direct Pb-Pb interaction within the overall cluster has not been established, but the distance between adjacent lead atoms falls in the range 344 to 409 pm (average 381 pm). The distance from the central O(1) atom to the four surrounding Pb(II) atoms ranges from 222 to 235 pm. The other Pb-O(H) distances the range is from 218 to 267 pm.

Lead azide, $Pb(N_3)_2$ is a well known primary explosive, and its structure was carefully investigated by three-dimensional neutron diffraction techniques [5,6]. There are four different types of azide structure in the unit cell. The azide groups are essentially linear but they differ in details of symmetry and also in spatial arrangement to the neighbouring atoms. The symmetric and

asymmetric azides are arranged in different layers and separated by a layer of Pb(II) atoms. Each lead atom is bonded to eight azide groups in a distorted tetragonal antiprismatic arrangement. The Pb-N distances range from 248 to 292 pm.

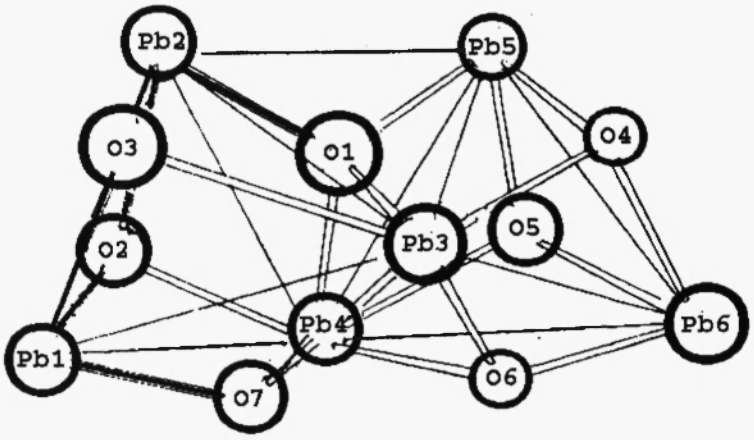

Fig.1. A View of the $[Pb_6O(OH)_6]^{+4}$ Complex [4]

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The structure of Pb(NCN) shows that the shortest Pb-N bond distances (233 to 251 pm) form continuous -Pb-N-Pb-N- spirals parallel to the *c* axis [7]. Identical spirals pack closely together along the *a* axis, being linked by weaker Pb-N bonds (257, 271 pm) in the form of closely packed sheets perpendicular to the *b* axis. The two shortest bonds from each lead atom are at an angle of 78.45° to each other, and a weaker Pb-N bond is almost perpendicular to both of these (ave. 88°).

In $Pb(NCS)_2$ [8] the Pb(II) atom lies on a two-fold axis and is surrounded by four nitrogen (mean Pb-N = 273.4(7) pm) and four sulphur atoms (mean Pb-S = 306.0(2) pm) which belong to eight different thiocyanate groups. The SCN unit is coordinated to two lead atoms through the nitrogen, and to two other lead atoms via the sulphur atom. The Pb-N and Pb-S distances all exceed the sums of the Pauling covalent radii of 228 and 262 pm, respectively. Therefore, these contacts can be considered more ionic than covalent in character.

There is a polymeric yellow lead(II) nitrite monohydrate [9] in which two independent Pb(II) atoms are found in the unit cell. The structure of lead(II) nitrate [10] is built up by a cubic face-centred type of arrangement of Pb(II) atoms, with nitrate groups in between, and perpendicular to the 3-fold axis, to give cubooctahedral 12-coordination by oxygen about Pb(II). Six of the twenty four edges of this distorted polyhedron are remarkably shorter than the others, and these are joined by nitrate groups.

Cerussite ($PbCO_3$) belongs to the aragonite-type group [11-13]. Each lead atom is surrounded by nine oxygen atoms (Pb-O range 258 to 278 pm). Each PbO_9 polyhedron shares three O-O edges with carbonate groups and six O-O edges with neighbouring PbO_9 polyhedra. The carbonate groups are slightly aplanar.

The composite layer in $2PbCO_3.Pb(OH)_2$ [14] is bounded top and bottom by planes of carbonate ions. Sandwiched between the carbonate groups is a puckered layer of hydroxy groups. Two planes of Pb atoms, in which identical lead atoms are in an almost undistorted hexagonal array, lie between the carbonate planes and the hydroxy layer, being closer to the former (Table 1).

There are three derivatives of the general formula $Pb_2X_2CO_3$ (X = F [16], Cl, or Br [17]). The crystal structure of the former [16] consists of endless spiral chains of edge-sharing FPb_4 tetrahedra extending in the *c* direction. These chains are joined by corner sharing to a three dimensional network of formula $(PbF)_n^{+n}$. The carbonate groups are situated in the tunnels formed by this network. The lead atoms are nine-coordinate. The PbO_5F_4 polyhedron was described as a very

distorted three-capped trigonal prism. The structure of the chloro and bromo derivatives [17] has two dimensional nets of Pb(II) and carbonate groups. In every quadratic mesh of the net there are two halide ions in mutual contact. The Pb atoms are nine coordinate, PbO_4X_5.

Crystals of $Pb_2(NO_2)(NO_3)(SeO_3)$, which were synthesised by partial reduction of nitrate ions with native copper under hydrothermal conditions [18], contain two non-equivalent Pb(II) atoms. Their coordination polyhedra are shown in Figure 2. The Pb1 atom is ten coordinate with oxygen atoms of all three anions (Pb-O range from 250.8 to 296.4(8) pm, ave. 276 pm). The Pb2 atom, coordinated only to oxygen atoms of SeO_3 groups, has three nearest oxygen atoms (Pb-O = 241(x1) and 245(x2) pm and six near oxygen atoms (280 to 322 pm).

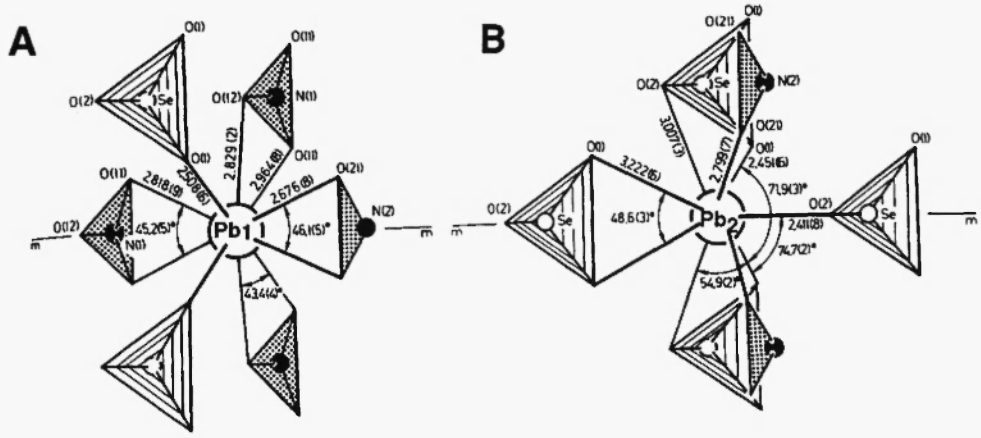

Fig.2. Coordination Polyhedra of $Pb_2(NO_2)(NO_3)(SeO_3)$ [18] (A) about Pb(1); (B) about Pb(2)

In lead apatite ($Pb_9(PO_4)_6$) [21] two crystallographically independent Pb(II) atoms are found. The Pb(1) atom is surrounded by nine O atoms (Pb-O = 252(1), 276(1) and 294(2), three of each). The Pb(2) atom is surrounded by six oxygen atoms at a mean distance of 257.0 pm. The edge length of the triangle formed by Pb(2) is 430.3(2) pm. The shape of the PO_4 tetrahedron is almost regular.

In the crystal structure of $Pb(H_2PO_4)_2$ [22] the Pb(II) atom is surrounded by seven O atoms (Pb-O = 244 to 288 pm) belonging to seven different $H_2PO_4^-$ groups. The coordination polyhedron is irregular, and by sharing the edges (O(3)-O(3) and O(8)-O(8)) the coordination polyhedra form infinite chains running in the *y* direction with a Pb-Pb separation 391.7 pm. This structure was also studied by another group of authors [23] with comparable results (Table 1). In $Pb(HPO_4)$ [23] the Pb(II) atom is six coordinated (Pb-O = 235 to 287 pm), the chains of edge linked PbO_6 polyhedra running parallel to the *z* direction.

The $P_3O_{10}^{-5}$ in $Pb_2HP_3O_{10}$ [25] anion consists of three PO_4 tetrahedra connected by common oxygen atoms. The chain has mirror symmetry across a plane passing the central P atoms. Lead(II) is coordinated by eight oxygen atoms. The polyhedra of Pb are connected parallel to *y* and *z* by common edges. Six $P_3O_{10}^{-5}$ chains are joined by one lead atom.

The $Pb_2P_4O_{12}$ derivative was prepared in three hydrate forms as di- [27], tri- [28] and tetrahydrate [29]. The structure of the dihydrate [27] consists of two crystallographically different $P_4O_{12}^{-4}$ ring anions, point symmetry i, connected by Pb and H-bonds. Both Pb(II) atoms are coordinated by eight oxygen atoms. The polyhedra of the lead atoms are interconnected by common edges forming sheets and chains. The Pb(1) atom is joined to four, and the Pb(2) atom to five $P_4O_{12}^{-4}$ ions. The structure of the trihydrate [28] contains cyclo-tetraphosphate anions with D_{2d} point symmetry with a square antiprism arrangement about the Pb(II) atom created by eight O atoms. The tetrahydrate [29] contains $P_4O_{12}^{-4}$ ring anion with point group symmetry i as in the dihydrate [27].

In $Pb_3P_4O_{13}$ [30] the $P_4O_{13}^{-6}$ anion is a linear linkage of four corner sharing PO_4 tetrahedra. There are three independent Pb(II) atoms with PbO_7 (x2) and PbO_8 chromophores linking these P_4O_{13} groups and building a three dimensional network.

The crystal structure of $PbAs_2O_4$ [32] consists of AsO_3 pyramids which are corner connected to form As_4O_8 rings of symmetry $\bar{1}$. The As_4O_8 rings are connected by the Pb(II) atoms to form a framework. The Pb(II) atom has four ligands with nearest Pb-O distances of 225 to 250 pm, and farther Pb-O distances of 310.4(10) pm.

The X-ray analysis of $Pb_3(AsO_4)_2$ [33] has a sandwich structure with two sheets of AsO_4 tetrahedra. The vertices point towards each other with a group of lead atoms (1) sandwiched in

TABLE 1. Crystallographic and Structural Data for Lead Inorganic Salts[a]

COMPOUND (colour)	Crystal SpGrpZ	a[pm] b[pm] c[pm]	α [°] ß [°] γ [°]	Chromophore		Pb-L [pm]	Pb-Pb[pm] Pb-L-Pb[°]		L-Pb-L [°]	Ref
$[Pb_3O(OH)_2]$	or	1081.4(5)		PbO_3	μ_1O^b	229(6)	381(-,37)	O,O'	not given	4
	Pbca	1670.6(6)		(x2)	μ_3HO	223(6,7)	O 109(-,11)			
$(ClO_4)_4.H_2O$	8	2627.3(8)		PbO_5	μ_4O	228(6,7)	HO 105(-,17)			
				(x2)	μ_3HO	256(6,46)				
(colourless)				PbO_3	μ_3HO	232(6,5)				
				PbO_4	μ_3HO	235(3,2)				
					H_2O	274(7)				
α-$Pb(N_3)_2$	or	1131		PbN_7	N	261(-,6)		N,N	74	5
	Pcmn	1625		(N_2)	(N)	287(-,4)			100, 129	
neutron	12	663		PbN_8	N	265(-,10)		N,N	68(-,1)	
diffraction				(N_4)	(N)	278(-,12)			78(-,1)	
									99, 128	
α-$Pb(N_3)_2$	or	663		PbN_7	N	248 -				6
	$Pna2_1$	1131		(N_4)	(N)	- 292				
neutron	12	1652								
diffraction										
Pb(NCN)	or	555.3(1)		PbN_6	N	233(4)	-	N,N	84.6(-,10.2)	7
	$Pna2_1$	1173.2(3)				254(7,3)	101.6(-,7.6)			
	4	386.7(2)				275(7,4)				
$Pb(NCS)_2$	m	966.1(4)		PbN_2S_2	μN	273.4(7,47)	-	N,N	74.4(2,8)	8
	C2/c	654.4(3)	92.37(2)		μS	299.6(2)	N 106.4(2)		142.0(2,6.1)	
(yellow)	4	825.3(3)				313.5(2)	S 144.2(1)	S,S	80.1(1,7.6)	
									141.4(1,2.9)	
								N,S	75.2(2,5.6)	
									115.1(2,5.8)	
									144.4(1)	
$Pb(NO_2)_2(H_2O)$	m	919.4(4)		PbO_{10}	H_2O	257.0(13)		not given		9
	$P2_1/c$	1180.6(5)	130.64(2)		O	254.3-298				
(yellow)	8	1221.0(5)				(ave. 274)				
				PbO_9N	H_2O	276.7(13)				
					O	258.3-292.9				
						(ave. 273)				
					N	275				

$Pb(NO_3)_2$	c	785.86(2)	PbO_{12}	O	274.82(6) x6					10
	Pa3				286.88(6) x6					
	4				(ave. 281)					
$PbCO_3$	or	516(6)	PbO_9	O	258-278					11
	Pmcn	846(8)			(ave. 270)					
(colourless)	4	614(6)								
$PbCO_3$	or	518.00(7)	PbO_9	O	262(4)			O,O	117.4	12
	Pmcn	849.2(3)			267(2,1)				125.2	
(colourless)	4	613.4(3)			274(2,3)					
$PbCO_3$	or	517.9(1)	PbO_9	O	259.4(1)			O,O	not given	13
(colourless)	Pmcn	849.2(3)			266.8(1,9)					
neutron	4	614.1(2)			274.0(1,24)					
diffraction										
$2PbCO_3.Pb(OH)_2$	trg	906	PbO_7	CO_3	273(-,23)	520				14
	P31m		(O_3)	HO	270					
(white)	?	827		(HO)	310					
			PbO_3	HO	240 x1					
electron			(O_5)		260 x2					
diffraction				(O)	340					
			PbO_7	CO_3	265(-,15)					
			(O_3)	HO	275					
				(HO)	330					
$PbCO_3.PbO.2H_2O$	hx	849	35.52	PbO_x	O	219	380			15
	R3m				(O)	322(-,4)				
(white)				PbO_5	CO_3	265				
electron										
diffraction										
$Pb_2F_2CO_3$	or	808.36(9)		PbO_2F_4	O	257(1,1)				16
	Pbcn	830.9(2)				293(1,6)				
	4	684.1(1)			F	255(1,17)				
$Pb_3Cl_2CO_3$	tg	813.9		PbO_4Cl_5	O	237, 268(-,5;				17
	P4/mbn				Cl	295, 326(-,18)				
	?	885.6								
$Pb_3Br_2CO_3$	tg	833.7		PbO_4Br_5	O	264(-,24)				17
	P4/mbn				Br	303, 333(-,18)				
	?	905.6								

$Pb_3(NO_2)(NO_3)$	or	552.9(2)		PbO_{10}	O	250.8-296.4(8) (ave. 276)		O,O	44.9(5,1.5)[c]	18
	$Pmn2_1$	1035.7(3)								
(SeO_3)	2	681.1(2)		PbO_9	O	243.8(7,27) x3 279.9-322.2(6) (ave. 282)		O,O	73.3(3,1.4)	
$Pb(PO_3)_2$	m	729		PbO_7	O	242-278 (ave. 258)		not given		19
	$P2_1/c$	795	90.5							
	8	1728		PbO_8	O	252-294 (ave. 264.5)				
$Pb_3(PO_3)_2$	m	1381.6(35)		FbO_5	O	262(3,1) x4 275(3,0) x2		not given		20
	C2/c	569.2(15)	102.36(5)							
	4	942.9(24)		PbO_{10}	O	233-289(3) (ave. 263)				
$Pb_9(PO_4)_6$	hx	982.6(4)		PbO_5	O	230-273(3) (ave. 273)	430.3(2)	not given		21
	$P6_3/m$									
(colourless)	1	735.7(3)		PbO_9	O	252-294(2) (ave. 274)				
$Pb(H_2PO_4)_2$	tr	902.9(3)	96.92(2)	PbO_7	O	244.4-288.0(14) (ave. 261)	391.7	not given		22
	P$\bar{1}$	586.3(1)	119.56(3)							
(colourless)	2	781.5(3)	104.92(2)							
$Pb(H_2PO_4)_2$	tr	782.3(1)	108.24(2)	PbO_7	O	242-289 (ave. 261)				23
	P$\bar{1}$	831.5(2)	96.90(2)							
(colourless)	2	585.6(2)	108.61(1)							
$Pb(HPO_4)$	m	468.4(1)		PbO_5	O	235-287 (ave. 257)				23
	Pc	664.2(1)	97.18(1)							
(colourless)	2	578.1(1)								
$Pb_2P_2O_7$	tr	691.4(2)	96.82(3)	PbO_7	O	243.2-299.4(14) (ave. 263)	396-453	O,O	109.4(8,5.9)	24
	P$\bar{1}$	696.6(2)	91.14(3)	(O)						
(colourless)	4	1275.1(4)	89.64(3)		(O)	320				
				PbO_3	O	243.4-304.4 (ave. 270)		O,O	109.4(8,5.4)	
				(O)	(O)	328				
$Pb_2HP_3O_{10}$	m	693(1)		PbO_3	O	247-309(10) (ave. 271)	420(-,10)	not given		25
	Cm	1434(1)	135.1(1)							
(colourless)	2	597(1)								

$Pb_3(P_3O_9)_2.3H_2O$	tg	1195.7(5)		PbO_5	O	259(2,4)			not given	26
	$P4_12_12$									
	?	1227.0(5)		PbO_7	O	259(2,21)				
					H_2O	272(2,12)				
$Pb_2P_6O_{12}.2H_2O$	tr	802(2)	98.8(2)	PbO_8	O	244-311			not given	27
	Pî	1058(2)	108.7(2)			(ave. 280)				
(colourless)	2	753(2)	82.6(3)	PbO_8	O	259-280(4)				
						(ave. 269)				
$Pb_2P_6O_{12}.3H_2O$	tr	786.4(3)	97.42(2)	PbO_8	O	248.1-290.5(10)			O,O 65.2-149.3(11)	28
	Pî	914.4(3)	100.63(2)			(ave. 268)				
(colourless)	2	1021.6(3)	114.92(2)	PbO_9	O	250.0-305.2(13)			O,O 66.2-149.6(13)	
						(ave. 269)				
$Pb_2P_4O_{12}.4H_2O$	m	807(2)		PbO_8	O	251-280			not given	29
	$P2_1/n$	1176(3)*	108.2(3)			(ave. 267)				
(colourless)	2	750(2)								
$Pb_3P_4O_{13}$	tr	783.0(5)	104.35(1)	PbO_7	O	244.2-295.0(7)			not given	30
	Pî	734.7(5)	101.81(1)	(x2)		(ave. 265)				
	2	1021.5(8)	94.27(1)	PbO_9	O	252.5-291.1(7)				
						(ave. 268)				
$Pb_5(PO_4)_3F$	hx	976.0(8)		PbO_9	O	247.5(16) x3				31
	$P6_3/m$					275.6(20) x3				
	?	730.0(8)				292.6(20) x3				
				PbO_4F_2	O	234.8(26)				
						256.7(18) x2				
						284.0(26)				
					F	296.1 x2				
$PbAs_2O_4$	m	703.7(3)		PbO_4	μO	225.0-250.0(8)	384.9(1)			32a
	$P2_1/c$	1180.1(6)	112.99(3)			(ave. 238.5)	107.5(4,1.5)			
	4	613.7(3)								
$Pb_5As_2O_5$	m	1358.4(4)		PbO_4	O	230.1-247.7(9)				32b
	$P2_1$	565.0(2)	108.78(2)	(O)		(ave. 238.0				
	4	855.1(3)			(O)	294.2(9)				
				PbO_4	O	226.0-254.5(9)				
				(O_2)		(ave. 243.6)				
					(O)	280.3(9)				
						305.5(9)				

$Pb_3(AsO_4)_2$	m	753.6		PbO_5	O	238.3-275.7	not given			33
	$P2_1/c$	602.9	115.15	(O_3)	(O)	311(-,9)				
	1	950.9		PbO_3	O	259.5-290.5 (ave. 270)				
$PbHAsO_4$	m	493.0(10)		PbO_x	O	240.2-283.6				34
	P2/c	677.2(16)	96.07(19)			258(ave)				
(colourless)	2	585.9(17)								
$Pb(AsO_3)Cl$	or	693.3(1)		$PbCl_4O_3$	Cl	283.0-340.8(4)				35
	$P2_12_12_1$	992.3(2)				311.7(ave)				
(colourless)	8	1137.4(2)			O	237(1,4)				
						277(1,1)				
$Pb_2(AsO_2)_3Cl$	or	536.8(1)		PbO_3Cl_2	O	234(2,1)				35
	Pmcn	818.9(3)			Cl	347(1)				
(colourless)	4	1951(1)		PbO_8Cl	O	259(1,10)				
						286(1,3)				
					Cl	310(1)				
$Pb_2(AsO_3OH)Cl_2$	m	641.0(2)		PbO_4	O	251.2(7,3)	O,O	62.5(3)		36
	$P2_1/m$	552.5(1)	90.69(2)	(Cl_4)	(Cl)	318.4(4,110)		73.1(3,2.1)		
(colourless)	2	929.3(3)						109.3(4,0)		
				PbO_2Cl	O	242.8(7,0)	O,O	74.0(3)		
				(OCl_5)	Cl	285.1(4)	O,Cl	80.2(2)		
					(O)	293.7(11)				
					(Cl)	320.0(7,140)				
$Pb_5(AsO_4)_3Cl$	m	1018.9(3)		PbO_9	O	240-318(3)				37
	$P2_1/b$	2037.2(8)				273(ave)				
(colourless)		746(1)	119.88(3)	PbO_6Cl_2	O	233-312(3)				
						271(ave)				
					Cl	315(2,5)				
	hx	1021.2(2)		PbO_9	O	273(2,23)				37
	$P6_3/m$									
		741.9(4)		PbO_6Cl_2	O	233-306(5)				
						268(ave)				
					Cl	314.6(1,0)				
$PbSO_4$		851.6(20)		PbO_8	O	263-293	O,O	48(-,1)[c]		38a
		539.9(10)		(O_4)		274(ave)		64(-,5)		
		698.9(10)			(O)	315(-,10)		82, 112		
								125		

PbO_2OSO_4	m	1376.9(5)		PbO_5	μO	230(3) x2	372(-,19)	μO,O	77.5(3,2.3)	38b
	C2/m	569.8(3)	115.56(5)	(O_4)	O	255(3)	109.6(3,7.3)			
(colourless)	4	707.9(2)				278(2) x2				
					(O)	308(3,1)				
				PbO_5	μO	231(3) x2		μO,O	78,7(3,1.0)	
				(O_4)	O	254(2)				
						282(1) x2				
					(O)	328(2,18)				
$Pb(S_2O_3)(H_2O)_4$	hx	634.13(9)		PbO_x	O	255(3)		not given		39
	P622					265(3,1)				
(colourless)	1	646.22								
$Pb_4(SO_4)(CO_3)_2$	m	911(2)		PbO_7	O	267(3,19)				40
	$P2_1/a$	2082(4)	90.46(2)	(O_3)	HO	221(3,6)				
$(OH)_2$	8	1159(3)			(O)	304-350				
(colourless)										
$Pb(ClO_2)_2$	or	600.4(1)		PbO_8	O	262.8(8,0)		not given		41
	Ccca	1250.4(2)				264.0(9,0)				
(yellow)	4	601.0(1)								
$Pb(ClO_3)_2(H_2O)$	m	881.1(1)		PbO_{11}	O	261.8-301.5(5)		O,O	106.5(3,1.6)	42
	C2/c	774.4(1)	93.13(1)			287(ave)				
	4	913.1(1)			H_2O	240.1(9)				
$Pb(BrO_3)_2(H_2O)$	m	895.2(1)		PbO_{11}	O	259.2-300.4(5)		O,O	104.1(3,1.6)	42
	C2/c	770.9(1)	92.20(1)			285(ave)				
	4	937.9(1)			H_2O	248.4(1)				
$Pb(IO_3)_2$	or	1670.4(3)		PbO_8	O	247.3(14,67)	412.8(1,67)	not given		43a
	Pbcn	557.8(1)				290.3(16,19)				
(yellow)	4	608.3(1)								
Pb(OH)Cl	m	1086.5(4)		$PbCl_2O_3$	HO	242.5(27,11)	376.5-			43b
	C2/m	400.6(2)	117.24(4)		Cl	324(-,20)	579.0(4)			
	?	723.3(3)								
Pb(OH)Cl	or			$PbCl_2O_3$	HO	241.2(7,57)	402.0-			43c
	Pcmn				Cl	324(-,10)	529.7(1)			
	?									

Footnotes: *a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.*

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Four membered metallocyclic ring.

between. The other group of lead atoms (2) lie almost in the same plane as the oxygen atoms forming the bases of the tetrahedra.

Both $Pb(AsO_2)Cl$ and $Pb_2(AsO_2)Cl$ derivatives [35] contain AsO_3 pyramids linked by common O atoms to single AsO_2 chains. The structure of the former is built up by formal AsO_2 vierer single chains which are connected by PbO_3Cl_4 polyhedra to a framework. In the structure of the latter $[Pb_2(AsO_2)_3Cl]$ the formal AsO_2 open-branched zweier single chains, and PbO_8Cl and PbO_3Cl_2 polyhedra are connected to layers parallel to the (001) plane.

Each of the two non-equivalent lead atoms in Pb_2OSO_4 [38] is coordinated to one side by three oxygen atoms (PbO_3 pyramids). The sulphate groups forms a nearly undistorted tetrahedron. The oxygen atom not belonging to the sulphate group is surrounded by a distorted tetrahedron of lead atoms. The lead tetrahedra share edges to form chains parallel to [010].

In yellow $Pb(ClO_2)_2$ [41] the Pb(II) and ClO_2 groups form two dimensional networks perpendicular to the b axis. The Pb(II) atom is surrounded by eight O atoms which form an Archimedean square antiprism (Pb-O, 262.8 and 264.0(9) pm).

From almost fifty lead inorganic salts in Table 1 only one [4] is a hexamer. All the rest are polymers with a wide range of chain arrangements. The Pb(II) atoms are found with various coordination numbers from three to twelve. As can be seen from the data, the predominant donor atom is oxygen. The Pb-O distances cover a wide range from 218 to 340 pm for those considered as the inner coordination sphere by the original authors. The mean Pb-O distance increases with coordination number as expected: 229 pm (PbO_3) < 245 pm (PbO_4) < 254 pm (PbO_5) < 260 pm (PbO_6) < 262 pm PbO_7 < 269 pm (PbO_8) < 272 pm (PbO_9) < 274 pm (PbO_{10}) < 281 pm (PbO_{11}, PbO_{12}). The Pb-Pb separations range from 340 to 520 pm, which rules out any consideration of metal-metal bonding in most cases, but there are also a number of structures for which the relevant data was not given.

3. DOUBLE AND HETEROMETALLIC LEAD SALTS

There are fifty heterometallic inorganic lead salts listed in Table 2 in the same order of their anions as Table 1, and in order of total number of metal atoms present. Some structural parameters, especially bond angles and metal-metal distances are not given in the original papers.

Crystals of $MPb(OH)_6$ [44], with Ca or Cd as the heterometal atom, are composed of $Pb(OH)_6^{-2}$ polyatomic ions with Pb-O bond distances of 217.0(9) pm (Ca) and 214.9(6) pm (Cd). The structure of the salt is that of NaCl, with the M-O bond distances of 236.0(9) pm and 232.7(6) pm, respectively.

The structure of pale yellow $K_2Pb[Pt(CN)_4].6H_2O$ [45] consists of zig-zag columns of planar $[Pt(CN)_4]^{-2}$ units (Pt-Pt distances 326.7(1) and 329.8(1) pm, Pt-Pt-Pt angles of 162.3(1)°. The Pb(II) and K(I) atoms sit in channels between the columns, and do not directly interact with the Pt atoms. Consequently the shortest Pb-Pt separation is 549.1(1) pm, ruling out any question of direct metal-metal interaction. The lead atom is surrounded by four water molecules (Pb-O = 245 to 280(1) pm) and two N atoms from the CN groups (Pb-N = 252 and 269(1) pm).

The structure of yellow $PbZn(NCS)_4$ [46] consists of *cis*-connected $[PbS_2S_{4/2}]$ moieties forming infinite two dimensional layers. All SCN groups are bound to Zn(II) by their N atoms. The resulting ZnN_4 tetrahedra are arranged in the cavities formed by the PbS_6 octahedra.

In a yellow PbRu double salt [47] the ruthenium atom exhibits pseudo-octahedral coordination. The hydroxy group occupies a position *trans* to the NO group, and the four NO_2 groups bind in *cis* positions to the ruthenium via nitrogen. The RuN_5O units are linked together by Pb(II) atoms and water of crystallization. The Pb(II) atom has contacts with virtually all of the oxygen atoms of the OH and NO_2 groups. The shortest Pb-O distances are 239 to 265(1) pm.

In yellow orange $K_2Pb(NO_2)_3(NO_3).H_2O$ [48] the Pb(II) atom has a quite irregular geometry arising from nine donor atoms from the NO_3 and two of the NO_2 groups. These ligands chelate to metal atoms in a bidentate fashion via their O atoms. The third NO_2 ligand acts as a bridge through two metal centres involving all three atoms.

There are several green-black $M_2PbCu(NO_2)_6$ derivatives where M = K [49-53], Rb [54], Cs [55-58] and Tl [59]. Each Cu(II) atom in all derivatives is coordinated by six N atoms of NO_2 ligands. The NO_2 groups are further coordinated to the Pb(II) atom as well as the M(I) atoms via oxygen atoms, resulting in eight coordination about Pb(II) and six coordination about M(I). The six nitro groups form a regular octahedron about Cu(II), or a tetragonally compressed environment with two short and four longer Cu-N bond distances. The reults have been interpreted in the original papers by invoking the Jahn-Teller theorem.

There are another two sets of compounds, $M_2PbCo(NO_2)_6$ (M = K or Rb [60]) and $K_2PbNi(NO_2)_6$ [61] which are all isostructural. In these, Co(II) or Ni(II) are surrounded by six NO_2 groups via nitrogen in octahedral environments.

TABLE 2. Crystallographic and Structural Data for Heterometallic Lead Salts[a]

COMPOUND (colour)	Cryscl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] ß [°] γ [°]	Chromophore	M-L [pm]	Pb-M [pm] Pb-L-M [°]	L-M-L [°]	Ref
$CaPb(OH)_6$	c	825.2(2)		$Pb^{IV}O_6$	O[b] 217.0(9)	130.92	O,O[b] 94.4	44
(colourless)	Pn3 4			$Ca^{II}O_6$	O 236.0(9)		O,O 93.6	
$CdPb(OH)_6$	c	815.0(2)		$Pb^{IV}O_6$	O 214.9(6)	130.07	O,O 94.57	44
(colourless)	Pn3 4			$Cd^{II}O_6$	O 232.7(6)		O,O 94.68	
$K_2Pb[Pt(CN)_4]_2.6H_2O$	m	648.7(1)		$Pb^{II}O_4N_2$	H_2O 262(1,18)	549.1(1)	O,O 85.7(4,4.8)	45
	$P2_1$	1792.8(2)	107.76(1)		CN 261(1,9)		147.9(4,4)	
(pale yellow)	2	931.6(2)					N,N 138.0(6)	
at 125K							O,N 75.1(5,7.5)	
							132.0(5,5.7)	
				$Pt^{II}C_4$	NC 200(2,4)	328.3(1,16)[c]	Pt,Pt 162.3(1)	
							C,C 90.0(7,2.2)	
							178.8(7,1.3)	
				KN_4O	CN 288(2,8)		not given	
					H_2O 270(1)			
				KN_3O_2	CN 286(1,10)		not given	
					H_2O 290(1,7)			
$PbZn(NCS)_4$	or	916.9(4)		$Pb^{II}S_6$	S 285(4,12)	-	S,S 88.0(5,7.0)	46
	$Pn2_1a$	606.1(3)			318(4,8)	174.4(8,9)		
(yellow)	4	2096.8(20)		$Zn^{II}N_4$	N 192(4,5)		N,N 65(2);105(2,3)	
$[PbR_3(NO)(NO_3)_4OH]$	or	1040.3(2)		$Pb^{II}O_2$	µHO 239(1)		µO,O 70.5(6,3.6)	47
$.0.5H_2O$	$Pc2_1n$	751.2(1)		(O_5)	ONO 259(2,6)		O,O 77.4-136.3(7)	
	4	1394.1(3)			(ONO) 289(2,14)			
(yellow)				RuN_5O	ON 174(1) x1		N,N 90.5(1,5.5)	
					O_2N 209(2,6)		171.0(1,2.0)	
					µHO 196(1)		N,µO 88.0(8,7.0)	
							177.0(1)	

$K_2Pb(NO_2)_3(NO_3).H_2O$	or	676.6(5)	$Pb^{[]}O_8N$	NO_3	268(2,15)	436(-,14)	O,O	45(1,1)[d]	48
	Pbca	1199.9(7)		O_2N	292(2)			63-167	
(yellow-orange)	8	2661(2)		NO_3	274(3,10) x2		O,N	66-178	
			KO_7	NO_3	291(2,8) x2	397.3(11)[c]	not given		
				NO_3	281(4,9) x3	435(1,2)[c]			
				H_2O	275(3,6) x2				
			KO_3	NO_2	282(3,18)		not given		
$K_4PbCu(NO_2)_6$	c	1068(2)	$Pb^{[]}O_3$	O	272				49
	Fm3		$Cu^{II}N_5$	N	203				
(green-black)	4		KO_6	O	313				
$K_2PbCu(NO_2)_6$	C		PbO_3	O	287				50
	Fm3		CuN_5	N	224				
(green-black)	4		KO_6	O	310				
neutr. diffr.									
$K_2PbCu(NO_2)_6$	c	1066(1)	PbO_3	O	279.4(5)				51
	Fm3		CuN_5	N	211.4(5)				
(green-black)	4		KO_6	O	311.6(5)				
neutr. diffr.									
$K_2PbCu(NO_2)_6$	c	1067.2(1)	PbO_3	O	279.3(3)				52
	Fm3		CuN_5	N	211.1(4)				
(green black)	4		KO_6	O	310.6(1)				
$K_2PbCu(NO_2)_6$	or	1074.1(1)	PbO_3	O	276.8(9,7)				53
	Fmmm	1073.4(1)	CuN_5	N	205.8(9) x2				
(green-black)	4	1053.8(1)			216.0(14,7)				
at 276K			KO_6	O	311.8(4,22)				
at 193K		1072.2(3)	PbO_3	O	276.4(11,23)				53
		1074.2(4)	CuN_5	N	207.1(14) x2				
		1050.8(3)			214.2(31,9)				
			KO_5	O	311.1(6,33)				

$Rb_2PbCu(NO_2)_6$[e]	or	1082.96(7)		PbO_3	O	279.3(3,15)	54
	Fmmm	1081.96(7)		CuN_5	N	206.3(4) x2	
(green black)	4	1061.13(7)				217.1(5,6)	
				RbO_5	O	314.7(1,21)	
				PbO_3	O	279.2(3,12)	
				CuN_5	N	206.3(4) x2	
						217.4(5,5)	
				RbO_5	O	314.9(1,20)	
$Cs_2PbCu(NO_2)_6$	or	1104(1)		PbO_3	O	285.5(9,6)	55
	Fmmm	1101(1)			N	207.1(6) x2	56
(green black)	4	1074(1)		CuN_6		223.0(7,3)	
at 293K				CsO_5	O	321.7(4,32)	
$Cs_2PbCu(NO_2)_6$	or	1102.6(6)		PbO_3	O	285.0(9,13)	56
	Fmmm	1100.3(6)		CuN_5	N	207.4(6) x2	
(green black)	4	1074.6(6)				222.4(8,3)	
at 323K				CsO_5	O	320.8(4,33)	
$Cs_2PbCu(NO_2)_6$	m	773.4(3)		PbO_3	O	285(2,4)	57
	B2/b	1553.1(6)	90.10(1)	CuN_5	N	209.4(7,21)	
	8	2137.6(8)				230.0(7) x2	
(green black)				CsO_5	O	319(2,1)	
neutr.diffrac.							
at 160K							
$Cs_2PbCu(NO_2)_6$	c	1097(2)		PbO_3	O	282.6(9)	58
				CuN_5	N	217.4(7)	
(green black)				CsO_5	O	322(1)	
at 420K							
$Tl_2PbCu(NO_2)_6$	c	1073.44(5)		PbO_3	O	280.2(3)	59
	Fm3			CuN_5	N	211.8(6)	
(green black)	4			TlO_5	O	313.5(2)	
$K_2PbCo(NO_2)_6$	c	1048.53(6)		$Pb^{II}O_8$	O	278.2(3)	60
	Fm3			$Co^{II}N_6$	N	202.4(4)	
(green-black)	4			KO_6	O	305.4(2)	
$Rb_2PbCo(NO_2)_6$	c	1061.16(8)		$Pb^{II}O_8$	O	281.4(2)	60
	Fm3						
(green-black)	4			$Co^{II}N_6$	N	204.6(3)	
				RbO_6	O	309.6(1)	

$K_2PbNi(NO_2)_6$	c	1057.75(8)		$Pb^{II}O_3$	O	277.3(2)							61
	Fm3			$Ni^{II}N_5$	N	208.0(2)							
(buff)	4			KO_6	O	308.2(1)							
$Pb_2CuO_2(OH)_2Cl_2$	m	1045.8		$Pb^{II}O_2Cl$	O	222(3,1)							62
	$P2_1/m$	575.0	97.79	(Cl_3)	HO	252(4,4)							
	2	669.3		x2	Cl	305(1,5)							
				$Pb^{II}O_4$	(Cl)	345.9							
				(Cl_4)	O	242(3,4)							
				CuO_4Cl_2	(Cl)	338(1,5)							
					HO	199(3,1)							
					Cl	296.6(17)							
$PbCu_3(OH)(NO_3)$	tr	776.1(3)	66.94(2)	$Pb^{II}O_7$	O	251.8(5,43)							63
	Pī	947.8(4)	69.83(3)	(O_1)		265.8(5,66)							
$(SeO_3)_3.0.5H_2O$	2	951.4(4)	81.83(2)	$Cu^{I}O_5$	(O)	312(1,13)							
					O	195.8(5,71)							
(green)						243.0(6,11)							
				$Cu^{II}O_5$	O	198.4(4,94)				O,O	79.5 - 97.7		
						244.9(4,133)							
$Pb_2Cu_3O_2(NO_3)_2$	or	588.4(2)		$Pb^{II}O_4$	O	244(3,16)	105(-,1)						63
$(SeO_3)_3$	$Cmc2_1$	1218.6(3)		(O_6)	(O)	309(4,11)							
(dark green)	4	1937.1(4)		$Cu^{II}O_4$	O	195(3,9)	112(-,14)[c]			O,O	90.0(-,5.7)		
$NH_4Pb(PO_3)_3$	m	721.4(2)		$Pb^{II}O_7$	O	239.9-282.9(10)	445.8(1,222)				not given		64
	$P2_1/c$	1706.2(3)	105.30(2)			(ave. 262)							
(colourless)	8	1415.7(2)		$Pb^{II}O_8$	O	242.0-296.4(10)							
						(ave. 269)							
$LiPb(PO_3)_3$	tr	724.5(3)	100.76(5)	$Pb^{II}O_8$	O	249.2-275.6(6)				O,O	72.8(1,6.7)		65
	Pī	740.9(3)	97.96(5)			(ave. 265)					134.5(2)		
(colourless)	2	679.5(3)	83.74(5)	LiO_4	O	204(1,11)				O,O	98.3(5,7.4)		
											158.0(5)		
$K_2Pb(PO_3)_4$	or	1551.0(1)		$Pb^{II}O_7$	O	244.8-296.5(11)							66
	Pbca	1555.0(1)				(ave. 262)							
(colourless)	8	924.9(1)		KO_8	O	287(1,27)							
				KO_{11}	O	303(1,35)							
$LiPb^{II}_2(PO_3)_5$	m	1228.9(10)		$Pb^{II}O_7$	O	245.1-292.7(4)	332(4,8)						67
	P2/n	968.9(8)	91.01(5)			(ave. 261)	552.3[c]						
(colourless)	2	552.3(5)											
				LiO_5	O	215(4,29)							

$LiPb^{II}PO_4$	or	794.5(6)		$Pb^{II}O_7$	O 234.6-302.3(9)	360(-,38)			68
	$Pna2_1$	1846(2)			(ave. 267)	309(2,11)[c]			
(colourless)	8	492.8(4)				109.0(7,1.7)[c]			
				LiO_4	O 194(2,14)				
$K_2Pb^{II}_8(PO_4)_6$	hx	982.7(1)		$Pb^{II}O_6$	O 223.8-267.3(12)	437.3	O,O	55.2(3)[d]	69
	$P6_3/m$				(ave. 256)			72.8-96.9(4)	
(colourless)	?	730.4(1)						152.2(3)	
				KO_9	O 253.3-292.4(10)				
					(ave. 276)				
$Nb^VOb^{II}_{11}(PO_4)_9$	c	1039.6(1)		Mo_6	O 233(3) x3		O,O	79.2(1,6.3)	70
	?				263(3) x3			114.7(1,0)	
	4/3							153.1(1,1)	
$Fe^{III}_2Pb^{II}(P_2O_7)_2$	tr	478.5(2)	89.71(2)	$Pb^{II}O_8$	O 248.9-319.7(6)	392.5(3)			71
	Pî	709.7(2)	87.53(3)		(ave. 276.7)				
(colourless)	1	785.1(3)	73.54(2)						
				$Fe^{III}O_5$	O 198.8(7,89)	785.5(3)[c]			
$Ni^{II}_3Pb^{II}(P_2O_7)_2$	m	742.1(1)		$Pb^{II}O_8$	O 256.9-274.2(6)		O,O	90.0(2,12.2)	72
	$P2_1/b$	945.6(1)			(ave. 266)			175.0(2,12.7)	
	2	767.8(2)	112.26(1)	$Ni^{II}O_6$	O 208.0(6,120)	318.4(3,33)[c]			
$Na_4Pb(P_3O_9)_2$	tr	726.8(4)	121.52(5)	MO_7	O 236.2-286.4(5)				73
	Pî	815.1(5)	102.06(5)		(ave. 267)				
	1	785.1(5)	73.00(5)	NaO_7	O 235.3-282.9(5)				
					(ave. 250)				
				NaO_5	O 235.9(5,4)				
					257.8(5) x2				
$Cs_3Pb_2(P_4O_{12})(PO_3)_3$	tr	680.8(5)	86.23(1)	$Pb^{II}O_7$	O 247.6-279.2(6)				74
	Pî	787.5(6)	96.96(1)		(ave. 260)				
	2	22.12(1)	113.98(1)	CsO_3	O 323.2(6,232)				
				CsO_9	O 326.9(6,206)				
$CuPbAsO_5$	tr	483.2(1)	78.68(2)	$Pb^{II}O_6$	O 233.4-294.5(7)	332.5(1)			75
	Pî	583.7(1)	74.95(1)		(ave. 255)				
(colourless)	2	799.5(2)	84.04(1)	Cu^IO_2	O 185.2(8,4)				
$CuPbAs_2O_7$	m	555.3(1)		$Pb^{II}O_8$	O 248.2-288.1(5)				76
	$P2_1/n$	840.4(1)	91.61(2)		(ave. 268)				
(blue)	4	1301.1(2)		$Cu^{II}O_5$	O 198.0(5,39)		O,O	74.5-107.9(2)	
					224.3(5)			156.1; 172.1(6)	

$CuPb_5(AsO_3)_2Cl_7$	tg	986.14(4)		$Pb^{[7]}O_3Cl_4$	O 236(1,3);297(1)			77
	R3	-			Cl 282.8-323.5(5)			
(colourless)	3	1708.9(2)			(ave. 309)			
				$Cu^{I}Cl_3As$	Cl 244(1,0)	Cl,Cl	112.5(2,0)	
					As 234(1)	Cl,As	106.3(2,0)	
$(NH_4)_2Pb(SO_4)_2$	inx	558(1)		$Pb^{[7]}O_6$	O 252			78
	R3m	-						
(colourless)	3	2184(5)						
$CuPb(SO_4)(OH)_2$	m	981		$Pb^{[7]}O_3$	O 244 x2	O,O	95.7	79
	$P2_1/m$	565	104.7	(O_3)	HO 238		105.9 x2	
	2	470			(O) 290(-,8)			
				$Cu^{II}O_5$	HO 195(-,3)	O,O	90.0(-,9.9)	
					O 253 x2			
$CuPb(SO_4)(OH)_2$	m	968(2)		$Pb^{[7]}O_3$	O 247 x2			80a
	$P2_1/m$	565(1)	102.36(15)	(O_2)	HO 236			
	2	468.5(10)			(O) 291(-,7)			
				$Cu^{II}O_6$	HO 195(-,2)	O,O	90.0(-,8.0)	
					O 247 x2			
$Na_3Pb_2(SO_4)_3Cl$	tg	9.81(2)		$Pb^{[7]}O_7Cl_2$	O 250-302			80b
	$P6_3/m$				Cl 304			
	?	714(2)		NaO_3	O 254(-,1);280 x3			
$Cu_3Pb(SeO_3)_3$	tr	781.3(1)	82.27(1)	$Pb^{[7]}O_7$	O 244.7-298.0(8)			81
	Pi	911.6(1)	72.90(1)	(O_3)	(ave. 260)			
(pale green)	4	1257.0(1)	89.69(1)		(O) 322(-,19)			
				$Pb^{[7]}O_8$	O 261.0-293.1(8)			
				(O)	(ave. 273)			
					(O) 317.4(8)			
				$Cu^{II}O_6$	O 192.2-312.9(8)	O,O	90.0(4,14.9)	
					(ave. 219)		162.9(4,10.8)	
$ZnPb(IO_3)_6.6H_2O$	tr	690.5(7)	97.2(1)	$Pb^{IV}O_6$	IO_3 207.0(2) x2	O,O	90.0(5,8.8)	82
	Pi	728.5(6)	104.15(8)		219.3(2,1)			
	1	1097.6(9)	88.11(8)	$Zn^{II}O_6$	H_2O 205.0(2,1)	O,O	87.5(6,4)	
					IO_3 221.7(2) x2			
$PbAl_2(CO_3)_2(OH)_4.H_2O$	or	908(1)		$Pb^{[7]}O_3$	CO_3 256(2,3)	O,O	47.7(7)[d]	83
	Pbnm	1637(2)			273(2)		57.9-159.3(7)	
(colourless)	4	562(1)			288(2,3)			
					HO 257(2)			
				$Al^{III}O_5$	CO_3 193(2,1) x2	O,O	90.0(1.0,9.7)	
					HO 188(2,3)		176.8(1.3,6)	

$CuPb_2(OH)_4Cl_2$	tg	587.0		$Pb^{II}O_4$	HO	247.7(12)	335.8	O,O	72.7(-,1.7)	84
	P4mm			(Cl_4)	(Cl)	332(2,11)			113.90(88)	
	?	549.7		$Cu^{II}O_6Cl$	HO	205.2(26)		O,O	88.92(20);164.2	
				(Cl)	Cl	254.8(19)		Cl,Cl	180	
					(Cl)	294.6(19)		O,Cl	90.0(-,7.9)	
$Cu_7Pb_5(SO_4)_3$	or	2008.9(7)		$Pb^{II}O_5$	O	246(-,1)				85
$(CO_3)(OH)_6$	$Pmn2_1$	714.6(3)		(O_4)		273(-,10)				
	2	656.0(5)			(O)	311(-,6)				
(blue-green)				$Pb^{II}O_8$	HO	242(-,12) x3				
				(O)	O	260;290(-,2)				
					(O)	355				
				$Pb^{II}O_3$	O	237(-,4) x2				
				(O_4)		270(-,4)				
					(O)	305-340				
				$Cu^{II}O_6$	HO	199(-,4) x4				
					O	240(-,4)				
$(CuZn)_3Pb(AsO_4)_2$	m	1014.7(2)		PbO_3	O	266.8-277.6(9)		O,O	58.0-134.4(3)	86
$(OH)_2$	C2/c	589.2(1)	106.05(1)			(ave. 272.2)			167.0(4,1.3)	
	4	1408.1(2)		CuO_5	O	200.0-245.4(9)	293.9(-,9)[c]	O,O	90.0(3,7.2)	
(dark-green)				(Zn)		(ave. 221)				
					HO	189.8(8,26)				
$(ZnFe^{+2},Fe^{+3})_2$	m	912.4(3)		PbO_3	O	259.4(-,3)				87
	C2/m	632.9(3)	115.17(2)			295.5 x2				
$Pb(OH)_2(H_2O)_2(AsO_4)_2$	2	757.7(2)		Zn/FeO_5	O	206.5(-,66)	316.5[c]			
$Cu_{20}Pb_{21}Cl_{42}(OH)_{40}$	tg	1506.5(2)		$PbCl_6$	Cl	284(2,6)				88
	I4/mmm	-		$PbCl_8$	Cl	291(1) x4				
	2	2443.6(5)				326(1) x4				
				$PbCl_6O$	Cl	283.5(7) x2				
						296.6(2) x2				
						313.2(7) x2				
					HO	260(3)				
				$PbCl_5O_2$	Cl	302.4(2) x2				
						308.4(7) x2				
						326(1)				
					HO	248(2,3)				
				$PbCl_6O_2$	Cl	294(1) x2				
						340.2(7) x4				
					HO	272(2)				
				CuO_6Cl_2	HO	196(2,3)				
					Cl	292.4(7,69)				
				CuO_4Cl	HO	196(1)				
					Cl	275(2)				

$Cu_{24}Pb_{31}Cl_{62}(OH)_{48}$	tg	1524(2)	$PbCl_5$	Cl	270.6(20,88)	335.2(6,3)		89
	I4/mmm	-	$PbCl_6$	Cl	276.8(11,124)	333.4(6)[f]		
	2	3074(15)	$PbCl_8$	Cl	303.1(9,276)	304.4(11)[f]		
			$PbCl_9$	Cl	323.4(18,231)			
			$PbCl_7O$	Cl	305.6(9,333)			
				HO	261(2)			
			$PbCl_4O_3$	Cl	303.3(7,131)			
				HO	276(2,2)			
			$PbCl_6O_3$	Cl	320.0(8,184)			
				HO	246(1,2)			
			CuO_4Cl_2	HO	195.5(10,5)	289.9(6,5)[c]		
				Cl	285.6(9,88)			
$Ag_9Cu_{24}Pb_{26}Cl_{62}(CH)_{48}$	c	1529	$PbCl_8$	Cl	299.5(20,55)	337(1)		90
	Pm3m		$PbCl_6O_2$	Cl	304(1,8)	490.2(7,2)[f]		
	5			HO	291(5,0)			
			$PbCl_6O_3$	Cl	318(2,12)			
				HO	263(6,0)			
			$AgCl_5$	Cl	272(3,2)	338[c]		
			$AgCl_6$	Cl	273(3,21)			
			CuO_4Cl_2	HO	200(4,11)	283[c]		
				Cl	288(3,3)	354[c]		
$La_{0.16}Nd_{1.18}Pb_{0.66}(CO_3)_2(OH)_{1.34}.0.66H_2O$	or	500.28(8)	MO_{10}	CO_3	257.3(17,7)		not given	91
	Pmcn	855.5(1)			270.4(16,44)			
	2	723.92(8)		HO x2	242.4(37,39)			

Footnotes:
a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. M-M distance; M-L-M angle.
d. Four membered metallocyclic ring.
e. There are two crystallographically independent molecules.
f. Pb-Pb distance.

The structure of chloroxylite, $Pb_3CuO_2(OH)_2Cl_2$ [62] consists of sheets of composition $[Pb_3CuO_2(OH)_2]^{-2}$ which are themselves made up of the layer sequence Pb-(O,OH)-Cu-Pb lying parallel to (101) , with two non-equivalent lead atoms.

There are two green $PbCu_3$ and Pb_2Cu_3 derivatives [63]. In the former, non equivalent Cu(II) atoms (CuO_5 and CuO_6) are linked by SeO_3 groups to give a three dimensional arrangement. The Pb(II) atom is surrounded by SeO_3 groups with seven to ten oxygen atoms around each lead atom (mean Pb-O distance = 262 pm for PbO_7, the additional oxygen distances average at 312 pm). In the latter of the two derivatives the two dimensional $[Pb_2Cu_3O_2(SeO_3)_2]$ sheets are connected only via Pb-O bonds ranging from 298 to 316 pm.

There are four colourless derivatives [64-67] in which $(PO_3)_n$ chains have a period of six- [64], three- [66] or five- [67] PO_4 tetrahedra and run along the *c* axis [65,67] or the *a* axis [66]. The Pb(II) and M(I) coordination polyhedra are connected to form a three dimensional framework.

In $LiPbPO_4$ [68] the three dimensional framework built up by LiO_4 and PO_4 tetrahedra sharing vertices and aligned along the *c* axis represents an uncommon arrangement. The Pb(II) atoms are distributed in the polyhedral cavities of this polar framework. Each Pb(II) atom is seven coordinate with Pb-O distances between 234.6 and 302.8(8) pm, and all are very distorted. The distortions are consistent with an unused lone pair of valence electrons on the lead atom.

The apatite structure, $A_6B_4(XO_4)_6Y_2$, is found for $Pb_8\ K_2(PO_4)_6$ [69] with the hexad anion site Y completely vacant. The 6h sites are occupied by lead alone, whereas the 4f sites are occupied in a 1:1 ratio by Pb and K atoms. A short Pb-O distance of 223.8(13) pm may explain the ability of bone mineral to incorporate and store lead atoms in the body. The presence of lone pairs of electrons from Pb(II) in the vicinity of the hexad site may explain why this site remains empty. Each Pb(II) atom is six coordinate (PbO_6) with a mean Pb-O distance of 256 pm and Pb-Pb separation in a triangle of 437.3 pm.

A view of $Fe_2Pb(P_2O_7)_2$ [71] is shown in Figure 3. The Fe(III) atoms occupy sites of distorted octahedral geometry and are arranged in two types of column. One has a -Pb-Fe-Pb-Fe- repeat unit (Pb-Fe separation of 392.5(3) pm), the other is all Fe atoms with an Fe-Fe separation of 785.1(3) pm. The Fe-O distances within these columns are in the ranges 194.3 to 207.1(6) pm and 193.5 to 207.7(6) pm, respectively. The Pb(II) atoms are eight coordinate (mean Pb-O = 276.7 pm) and the P_2O_7 groups have an eclipsed conformation.

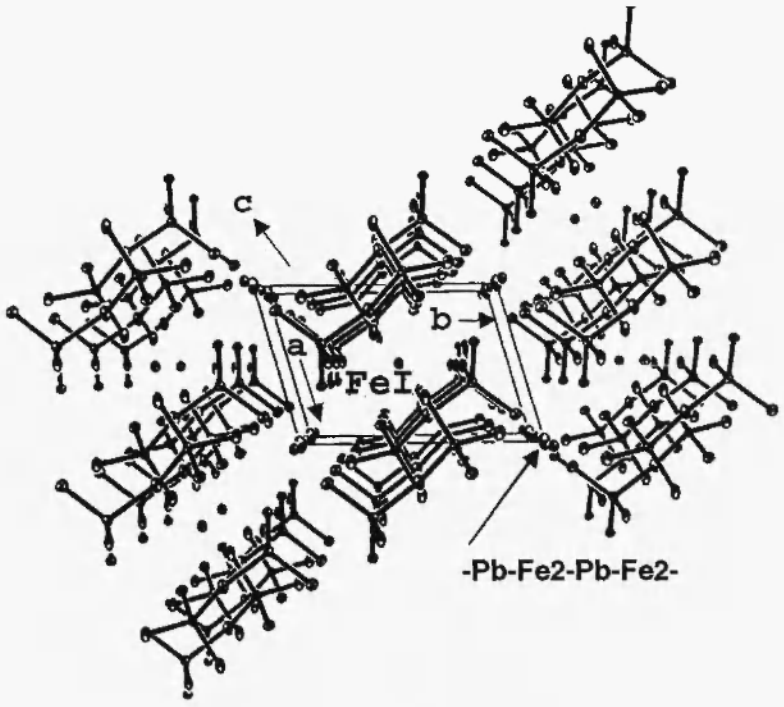

Fig.3. View of $PbFe_2(P_2O_7)_2$ [71]

In blue $PbCuAs_2O_7$ [76] the Pb(II) atom is irregularly eight coordinate PbO_8 (mean Pb-O = 268 pm) and the Cu(II) atom is tetragonal pyramidal CuO_5 (mean Cu-O_{eq} =198.0 pm, Cu-O_{ap} =

224.3(5) pm). Each pair of AsO_4 tetrahedra share a common O atom corner, building up As_2O_7 groups. These groups are connected with the CuO_4 polyhedra to sheets parallel (l01). These sheets are combined by the PbO_8 polyhedra to a framework.

A partial view of dundasite $[PbAl_2(CO_3)_2(OH)_4.H_2O]$ structure [83] is shown in Figure 4. The structure consists of a three dimensional framework of coordination polyhedra around Pb^{II}, (PbO_9), and Al^{III}, (AlO_6).

The structure of dark-green bayldonite $(Cu,Zn)_3Pb(AsO_4)_2(OH)_2$ [86] consists of interconnected octahedral Cu layers and lead arsenate polyhedral-tetrahedral layers which alternate along the *c* axis, giving rise to complex pseudo-hexagonal layers parallel to [001]. The Cu(II) octahedral sheet, with six membered octahedral rings, is formed by three crystallographically independent $[CuO_4(OH)_2]$ octahedra with point symmetry 1, showing Jahn-Teller distortion. The $Pb^{II}O_8$ polyhedron is a square antiprism with an average Pb-O distance of 272.2 pm.

The structure of tsumeorite, $Pb(Zn,Fe^{II},Fe^{III})_2(OH,H_2O)_2(AsO_4)_2$ [87] consists of layers of $[(Zn,Fe)(OH,H_2O)AsO_4]^-$ ions parallel to the *ab* plane, formed by coordination octahedra around Zn and Fe and AsO_4 tetrahedra via shared edges and corners. The Pb(II) atoms occupy special positions with site symmetry i between these layers. The PbO_8 coordination polyhedron is a distorted tetragonal prism.

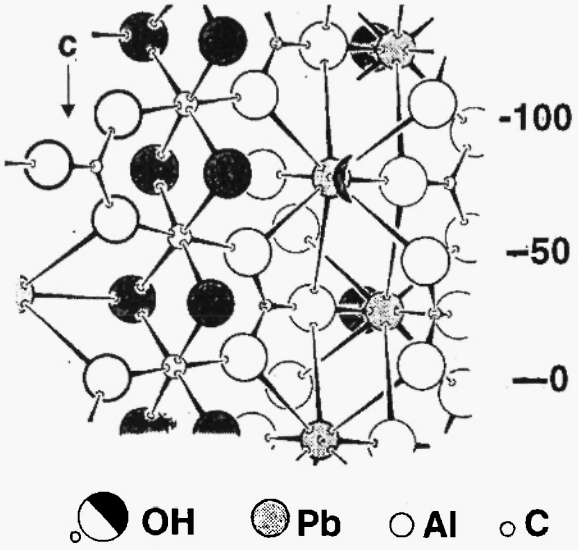

Fig.4. View of $PbAl_2(CO_3)_2(OH)_4.H_2O$ [83]

The structure of cumengeite [88], pseudoboleite [89] and boleite [90] are shown in Figure 5. The structure of pseudoboleite (Fig. 5B) may be seen as intermediate between boleite (Fig. 5A) and cumengeite (Fig. 5C). The main difference between the first two structures (A and B) in Figure 5 is the incomplete occupancy in pseudoboleite by lead of the sites which are occupied by silver in boleite. The structure of cumengeite may be derived from pseudoboleite by removing from each unit cell four sheets of atoms parallel to [001] as well as two further sites (Pb and Cl), and leaving the rest of the structure essentially unaltered. A more detailed account is available in the original paper for pseudoboleite [89].

The data in Table 2 reveal that of the fifty examples in this section only three contain Pb(IV) atoms [44,82] with the heterometal atom being calcium or cadmium [44] and zinc [82], and no transition metal examples. Each Pb(IV) atom is six coordinate (PbO_6) with a mean Pb-O bond distance of 216 pm (range 207 to 219 pm), and no Pb-M bonding.

In the series of double salts and heterometallic lead(II) salts, both transition and non-transition metal and also lanthanum atoms are found. When the second metal is Li, K, Ca, Cd, Cu(I) or Al, the compounds are colourless. Those with Cu(II), Co(II) and Ni(II) are green (blue); those of Zn, Pt or Ru are yellow.

The most common donor atom is oxygen (Pb^{II}-O distance from 228(3) to 360 pm). The most common coordination number about Pb(II) is eight with square antiprismatic geometry. The mean Pb-O distance increases in the order of coordination number: 253 pm (six-) < 263 pm (seven-) < 276 pm (eight-) < 277 pm (nine-) < 280.5 pm (ten- PbO_{10}). The mean Pb(II)-O distance of 253 pm for $Pb^{II}O_6$ is about 37 pm longer than that for $Pb^{IV}O_6$ (216 pm), as expected.

Metal-metal distances found in these salts (Table 2) increases in the sequence: 332.5 pm (M = Cu(I)) , 336 pm (Cu(II)) < 346 pm (Li(I)) < 392.5 pm (Fe(III)) < 436.5 pm (K(I)) < 549 pm (Pt). The Pb-Pb distances range from 304.4 to 490.7 pm, some of which are therefore within bonding range. The M-M distances are: 283-294 and 354 pm (M = Cu); 309 pm (Li) < 318 pm (Ni) < 328 pm (Pt) < 338 pm (Ag) < 397 pm (K) < 785.5 pm (Fe); and Fe-Ni is 316.8 pm.

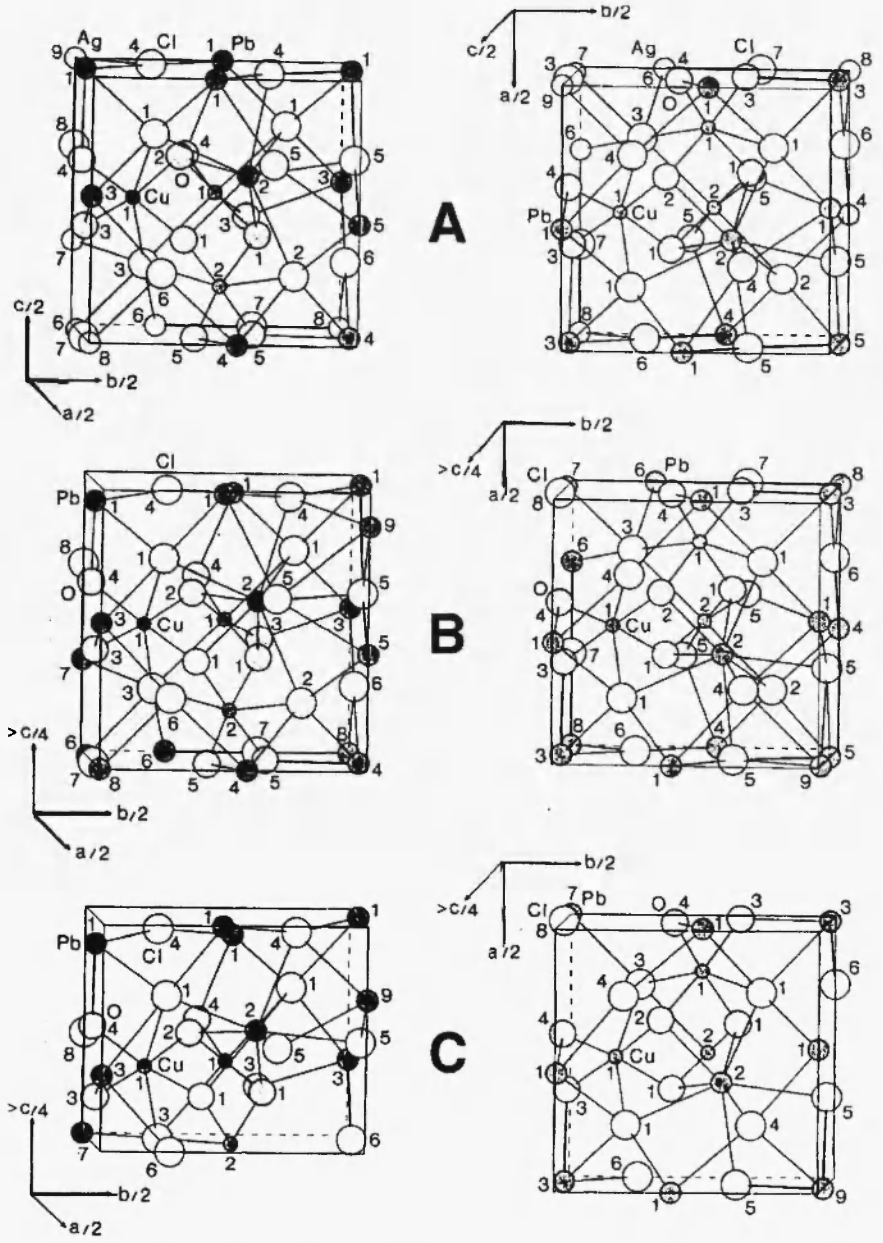

Fig.5. Tilted (4°) [100] Projections (left) and [001] Projections (right) of the Crystal Structures of: (a) Boleite [$Pb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$ [90]; (b) Pseudoboleite [$Pb_{31}Cu_{24}Cl_{62}(OH)_{48}$]; [89] (c) Cumengeite [$P_{21}Cu_{20}Cl_{42}(OH)_{40}$]; [88] *(The numbers of atomic sites reported have been changed into those of pseudo-boleite to facilitate comparison between structures. Pb(6) to Pb(9) sites are occupied by Ag in boleite.)*

4. LEAD HALIDES

The structural data for over sixty lead halides are presented in Table 3. There are two oxidation states possible in the lead halides giving rise to PbX_2 and PbX_4 derivatives. The former are

TABLE 3. Crystallographic and Structural Data for Lead Halides[a]

COMPOUND (colour)	Cryscl Sp.Grp Z	a[pm] b[pm] c[pm]	α [°] ß [°] γ [°]	Chromo-phore	Pb-L [pm]	Pb-Pb [pm] Pb-L-Pb [°]	L-Pb-L [°]	Ref
PbF_2 (gas) elect. diffr.				PbF	F[b] 213	F,F[b]		92a
PbF_2 (colourless)	or Pmnb 4	388.9(2) 642.8(3) 763.3(4)		PbF_7 (F_2)	F 248-282 (ave. 260) (F) 284			93
PbF_2 elect. diffr. (colourless)	or Pnma 4	644.0 389.9 765.1		PbF_7 (F_2)	F 241(2)-269(1) (ave 255) (F) 303(1)			94
$PbCl_2$ (gas) elect. diffr.				PbCl	Cl 246			92a 92b
$PbCl_2$ (colourless)	or Pnam 4	763 453.5 905		$PbCl_7$ (Cl_2)	Cl 281-331 (ave. 304) (Cl) 345			95
$PbCl_2$ (colourless)	or Pnam 4	762 905 453.5		$PbCl_7$ (Cl_2)	Cl 286-308 (ave. 299) (Cl) 364			96
$PbCl_2$ neutr. diffr. (colourless)	or Pnam 4	761.5 451.4 902.2		$PbCl_7$ (Cl_2)	Cl 285.4-308.1 (ave. 299) (Cl) 363.6			97
$PbBr_2$ (gas) elect. diffr.				PbBr	Br 260			92a 92b
$PbBr_2$ (colourless)	or Pnam 4	471.5(10) 802(1) 948.5(10)		$PbBr_7$ (Br_2)	Br 299-330 (ave. 314) (Br) 385			98a
PbI_2 (gas) elect. diffr.				PbI PbI	I 278 - I - 279			92a 92b
PbI_2 (yellow)	hx P3m1 1	455.7 697.9		PbI_6	I 321.6	455.7		98b

$(MeNH_3)[PbCl_3]$	c	565.7(2)		$PbCl_6$	μCl	283				99
(colourless)	Pm3m									
	1									
$[NH_3(Pr)]_2$	or	781.5(1)		$PbCl_6$	μCl	283.0-291.1(7)				100
$[PbCl_4]$	Pnma	2503.4(3)				(ave. 287.9)				
(colourless)	4	795.4(1)								
Cs_2PbCl_6	m	1344.9(1)		$PbCl_6$	Cl	288.6(3,4)		Cl,Cl	90.0(1,4)	101
	B2/b	941.7(1)							180	
	?	1318.1(1)	91.61(5)							
$(NH_4)[Pb_2Cl_5]$	m	901.8(3)		$PbCl_7$	Cl	287-316(1)				102
	$P2_1/c$	798.1(6)	90.09(2)			(ave. 296)				
(colourless)	4	1250.2(4)		$PbCl_8$	Cl	291.5-338(1)				
						(ave. 305.5)				
$(NH_4)[Pb_2Cl_5]$	m	900.4		$PbCl_x$	Cl	290-319				103
	$P2_1/c$	797.3	90.0							
(colourless)	4	1249.2								
$[Pb_2Cl_5]$	m	1053.2(2)		$PbCl_5$	Cl	not given				104
$[Co(N\text{-}Meen)_2$	$P2_1/n$	1512.6(5)	109.10(2)							
$(ox)].2H_2O$ (red)	4	1456.4(3)								
$[H_2N(CH_2)_2NH_3]$	or	940.2(3)		$PbCl_4$	μCl	293.6(4,37)	380.0(2)	not given		105
$[Pb_2Cl_6]$	Pbcm	1606.8(4)		(Cl_4)	Cl	272.3(4,41)	432.2(1)			
	8	1688.7(15)			(μCl)	325(-,46)	448.0(2)			
(colourless)				$PbCl_8$	μCl	300.9(4,89)		not given		
$[Co(en)_3]_2$	m	1158.0(28)		$PbCl_6$	μCl	291.5(10,73)	429.1	μCl,μCl	85.7(2,9.1)	106
$[Pb_2Cl_9]Cl.3H_2O$	$P2_1/m$	1470.9(1)	91.03(1)		Cl	280.7(10,72)			162.8(2,7)	
	2	1125.4(6)				300.2(11,70)		μCl,Cl	90.8(2,12.4)	
(orange-brown)									166.7(2,1.3)	
								Cl,Cl	89.8(2,6.0)	
									175.6(2,1.1)	
$[Co(en)_3]_2$	m	1160(2)		$PbCl_6$	Cl	278-304				107
$[Pb_2Cl_9]Cl.3H_2O$	$P2_1$	1474(3)	91.0(3)							
	4	1129(2)								
(orange-brown)										
$[Co(NH_3)_6]$	m	2065.8(3)		$PbCl_7$	Cl	291.3(6,31)		Cl,Cl	64.7-157.0(2)	108
$[Pb_4Cl_{11}]$	C2/c	776.2(2)	114.58(1)			307.2(6,83)				
	4	1617.1(1)		$PbCl_7$	Cl	295.9(7,32)		Cl,Cl	66.8-153.9(2)	
(red)						322.8(6)				

$(NH_4)_2PbCl_6$	c	983.4(2)	$Pb^{IV}Cl_6$	Cl	248						109
–											
(yellow)	4										
K_2PbCl_6	c	972.5(2)	$Pb^{IV}Cl_6$	Cl	233						109
–											
	4										
Rb_2PbCl_6	c	1019.8(3)	$Pb^{IV}Cl_6$	Cl	250						109
–											
	4										
Cs_2PbCl_6	c	1041.6(2)	$Pb^{IV}Cl_6$	Cl	250						109
–											
	4										
$(MeNH_3)PbBr_3$	c	590.2(2)	$PbBr_6$	μBr	296						99
	Pm3m										
(orange	1										
K_2PbBr_4	m	860	$PbBr_6$	μBr	286-304				Br,Br	90.0(-,10.7)	110
	$P2_1/a$	1300									
(colourless)	?	460									
$K_2PbBr_4.H_2O$	or	858.7	$PbBr_6$	μBr	297.5(1) x2	459.4			Br,Br	90.0(1,8.0)	111
	$P2_12_12$	1308.3			304.0(5) x2					179.6(2,1)	
(colourless)	2	459.4			306.9(5) x2						
$[PbBr_4]$	or	853.2(6)	$PbBr_6$	Br	288.2-				Br,Br	90.8(1,11.2)	112
$[Pb(tasn)]$	$P2_12_12_1$	1000.1(4)			320.6(2)					166.8(1,4.2)	
(colourless)	4	1860(1)			(ave. 302.2)						
$NH_4[Pb_2Br_5]$	tg	839	$PbBr_8$	Br	289-335	374(5)					113
	I4/mcm				(ave. 319)						
(colourless)	4	1434									
$Rb[Pb_2Br_5]$	tg	841	$PbBr_8$	Br	289-339(5)	376(5)					113
	I4/mcm				(ave. 321)						
	4	1450									
$(MeNH_3)[PbI_3]$	c		PbI_6	μI	315						99
	Pmcm										
(black)	1										
$(NMe_4)[PbI_3]$	hx	978.2(1)	PbI_6	μI	322.3(1,0)	395.8(1)			μI,μI	86.25(1)	114
	$P6_3/m$					75.76(1)				93.75(1)	
(pale yellow)	2	791.67(8)								180.0	

(pipH)[PbI_3]	or	869.1(1)		PbI_5	μI 322.7(4,29)	406.3(1)	μI,μI 90.4(1,7.1)	115
	$C222_1$	1839.2(2)				78.0(1,2)	178.8(1,7)	
(pale yellow)	4	812.49(4)						
(quH)[PbI_3](qu)	m	1373.0(3)		PbI_6	(μ)I 317.1-	402.3(1)	not given	116
	$P2_1/n$	804.3(I)	94.17(1)		329.2(1)			
(pale yellow)	4	1998.6(3)						
(Me_4enH)[PbI_3]	m	1078.2(1)		PbI_6	μI 322.4(1,44)	397.9(1)	μI,μI 90.0(1,5.8)	117
	$P2_1/c$	1777.5(3)	99.38(1)			not given	177.6(1,1.3)	
(colourless)	4	795.8(2)						
(hmtaH)[PbI_3]	m	1141.9(6)		PbI_6	μI 323.0(2,45)	383.5(1)	μI,μI 90.0(1,2.3)	118
	$P2_1/m$	944.1(2)				72.8(1,1.1)		
(colourless)	2	766.9(3)	110.63(3)					
NH_4[PbI_3].$2H_2O$	or	1026.2(2)		PbI_6	μ_3I 333.2(1,130)		I,I 90.0(1,3.3)	119
	Pnma	461.1(1)			μI 322.0(1,0)		176.0(1,1.0)	
(pale yellow)	4	2261.3(5)			I 302.5(1)			
K[PbI_3].$2H_2O$	or	1016.8(2)		PbI_6	μ_3I 332.6(1,135)	455.7	I,I 90.0(1,4.0)	119
	Pnma	457.7(1)			μI 321.1(1,0)		176.0(1,1.0)	
(pale yellow)	4	2248.4(5)			I 303.2(1)			
Rb[PbI_3].$2H_2O$	or	1027.6(5)		PbI_5	not given			119
	Pnma	471.5(3)						
(pale yellow)	4	2262.3(9)						
Rb[PbI_3]	or	1027.4(1)		PbI_6	μ_3I 338.2(2)	477.3	μI,μI 84.5(1,4)	120
	Pnam	1738.1(2)			μI 323.9(1,15)		92.5(1,0)	
	4	477.3(1)			I 303.7(2)		176.45(7)	
$CsPbI_3$	or	479.5		PbI_6	μ_3I 342	479.7		121
	Pnma	1045			μI 325(-,2)			122
(black)	-	1776			I 301			
$\{Ph(CH)_2NH_3\}_2$	m	3250.8(5)		PbI_6	μI 316.8(1,10)	-	μI,μ1 89.45(3)	123
[PbI_4]	C2/m	613.1(1)	93.80		I 320.4(1)	152.8(4,6)	180	
at 203K	?	618.5(1)					μI,I 89.8(1,1.1)	
(orange)							I,I 180	
$(C_5H_{15}NH_3)_2$	or	903.4(1)		PbI_5	μI 320.0(1,6)	627.4(1)	μI,μI 87.76(3)	124
[PbI_4]	Pbca	870.8(1)			I 319.8(2)	92.2	μI,I 87.5(1,1.0)	
(dark orange)	4	3978.5(3)						

$(NH_2C(I)NH_2)_3$	m	642.40(5)		PbI_6	μI	321.3(3,31)	-	μI,μI	177.24(9)	125
$[PbI_6]$	$P2_1/c$	2008.7(2)	92.906(8)		I	321.4(3,73)	177.2(1)	μI,I	90.0(1,3.0)	
(yellow)	4	1875.2(2)						I,I	90.0(1,7.3)	
									174.2(1,1.5)	
$(Ph(CH_2)_2NH_3)_2$	tr	879.4(1)	94.02(1)	PbI_6	μI	317.5(2,14)	-	μI,I	90.0(1,3.8)	123
$(MeNH_3)[P_2I_7]$	Pī	879.2(1)	97.02(1)			326.7(3,5)	155.9(1,1.0)		177.1(1,1)	
(orange)	?	2276.6(2)	90.18(1)		I	313.4(3,4)	180(1)			
$K_3[Pb_2I_8].4H_2O$	tg	1318.3		PbI_6	μI	323.5(1) x4		μI,μI	90.9(3)	126
	P4/nnnm				I	321.4(1) x2				
(black)	2	453.9								
PbFCl	tg	409(1)		PbF_4Cl_5	F	255 x4	409;414;514			127
	-				Cl	308 x4				128
(colourless)	2	721(2)				320				
$6PbF_2.PbCl_2$	hx	1027.4(1)		PbF_9	F	248(1) x3				129
	P6					274(1) x5				
	1	398.75(5)		PbF_2Cl_2	F	243(1,2) x4				
						277(1)				
						300(1) x2				
					Cl	316.7(2) x2				
				PbF_2Cl_2	F	255(1,9)				
					Cl	321.9(2)				
$5PbF_2.PbBr_2$	m	728		PbF_3	F	258(2,2)	403.0(4)			130
	-	425	96.40	PbF_4Br_3	F	248(2,10)				
	1	2217		(F_3)	Br	334.2(4,13)				
					(F)	284(-,2)				
$Na_2Pb_{11}F_{16}Br_6$	hx	1429.4(1)		PbF_2Br_4	F	244.9(13,42)	397.3(1)			131
	$P6_3/m$				Br	324.6(2,38)				
	?	401.35(5)		PbF_7Br_2	F	235.9-273.2(13)				
						(ave. 258.5)				
					Br	339.0(2)				
$4PbF_2.PbI_2$	or	431.35(2)		PbF_4I_3	F	255(-,12)	381(1)			130
	-			(F_3)	I	336(1,2)				
	3	5806.7(4)		x2	(F)	294(-,2)				
				PbF_5I_3	F	269(3,7)				
					I	372(2)				
				PbF_3	F	252(8,2)				
						267(8)				
				PbF_4I_3	F	248(1,7)				
					I	370(2)				

$5PbF_2.PbI_2$	or	743.36(8)	PbF_3	F	258(4,2)	404.2(2)	130
	Ccmm	426.67(4)	PbF_6I_3	F	237-292		
	1	2283.8(2)			(ave. 262.5)		
				I	352.1(7,2)		
$7PbF_2.PbI_2$	or	607.11(6)	PbF_3	F	260(4,9)	391.1(5)	130
	Bmmb	601.98(5)	$(F_2.$	(F)	305(1)		
	2	2508.4(2)	PbF_5I_4	F	218(9)		
					239(4) x3		
				I	384.1(6,11)		
			PbF_8	F	268(4,12)		
			(F_3)	(F)	303(9,3)		
			PbF_4I_4	F	242(4) x4		
				I	335.0(6) x2		
					356.9(6) x2		
PbClBr	or	786.4	$PbCl_4Br_3$	Cl	289.8(10) x2		132
	Pnam	920.9	(Br_2)		309.7(10,54)		
(colourless)	4	457.8		Br	306.5(5)		
					322.3(5)		
				(Br)	354.8(5) x2		
PbClI	or	881.8(8)	$PbCl_4I_2$	Cl	291.3(8)		132
	Pnam	964.5	(I_3)		297.4(8) x2		
	4	459.5			326.5(8)		
				I	336.7(3) x2		
				(I)	354.2(3,22)		
PbClI	or	818.7	$PbCl_4I_3$	Cl	293.1(3)		133
	Pnam	965.4	(I_2)		296.0(2) x2		
	4	459.3			333.0(4)		
				I	337.3(1,17)		
				(I)	352.7(1) x2		
PbBrI	or	867.4	$PbBr_4I_4$	Br	299.0(4)		132
	Pnam	1048.3			314.5(4)		
	4	444.8			339.3(4)		
				I	318.8(3)		
					367.5(3) x2		
PbBrI	or	1045.2(1)	$PbBr_4I_4$	Br	298.0(2)		133
	Pnam	863.9(1)			312.8(1) x2		
	4	442.7(1)			339.1(2)		
				I	317.5(1) x2		
					365.6(1) x2		

Footnotes: a. and b. see Table 1

more common, as can be seen from the Table. The PbX_2 series (X = F, Cl or Br) all form colourless orthorhombic crystals [93-98] in which Pb(II) is surrounded by nine halide atoms at the corners of a tricapped trigonal prism. There are never nine equidistant X atoms, but rather a range of distances in which one can discern seven shorter (mean Pb-X = 257 pm (F) < 300 pm (Cl) < 314 pm (Br)) and two longer (mean Pb-X = 293.5 pm (Cl) < 358 pm (Cl) < 385 pm (Br)) distances. The iodide derivative PbI_2 is yellow and has the cadmium iodide hexagonal layer lattice structure, and exists in several polytypes [98b]. The PbX_2 gas phase interatomic distances [92] are much shorter because of increased covalency. The values reflect the covalent radii of the halide atoms and increase in the order: 213 pm (F, 58 pm) < 246 pm (Cl, 99 pm) < 260 pm (Br, 114 pm) < 278 pm (I, 133 pm).

The cubic $(CH_3NH_3)PbX_3$ structures, where X is Cl, Br or I [99], are unusual in certain respects. Their colour intensity changes from the cream white chloride to the red-orange bromide and black iodide as charge transfer absorption moves into the visible range. The methylamine cation is nominally at the centre of a simple cubic cell and inside a cubooctahedral edge formed by twelve nearest halide neighbours. Each Pb(II) atom is surrounded by six X atoms with mean Pb-X distances which follows the covalent radius of the X atom in the sequence: 283 pm (Cl) < 296 pm (Br) < 315 pm (I).

The colourless $(NH_3Pr)_2[PbCl_4]$ unit crystallizes in a perovskite type layer structure [100]. The Cl atom octahedra centred by Pb atoms form infinite two dimensional layers which are sandwiched between the propylammonium chains. In Cs_4PbCl_6 [101] the Pb(II) atom is six coordinate with a regular octahedral arrangement ($PbCl_6$) with mean Pb-Cl distance of 288.6(3) pm and Cl-Pb-Cl bond angles of 90.0° (*cis*) and 180° (*trans*).

There are three species [102-104] which contain $[Pb_2Cl_5]^-$ anions. In two of these [102,103] the Pb(II) atoms are non-equivalent ($PbCl_7$ and $PbCl_8$, respectively), in the third both lead atoms are five coordinate ($PbCl_5$).

In the latter case the $[Co(N\text{-}Meen)_2(ox)]^+$ cation and the water molecules are in cages formed by the infinitely polymerised $(Pb_2Cl_5)_n$ units [104]. The two Pb(II) atoms are linked to each other by three bridging chlorine atoms to raise the coordination number of Pb(II) to five. The coordination geometry was described as a distorted octahedron with one open position.

In colourless $\{H_3N(CH_2)_2NH_3\}[Pb_2Cl_6]$ [105] the Pb(II) atoms are eight coordinated. The coordination polyhedra may be described as distorted bicapped trigonal prisms around the Pb(1) and Pb(3) atoms, with Pb-Cl distances ranging from 268.3(3) to 371.4(4) pm (mean, 308.5 pm). The Pb(2) atom is in a square antiprism, with Pb-Cl distances from 292.0(3) to 306.0(4) pm (mean, 300.9 pm). The polyhedra are linked by sharing faces to infinite layers running parallel to the *bc* plane. The ethylenediammonium cations, located between the layers, are linked via hydrogen bonds to the chloride ions.

In the orange-brown derivative [106,107], shown in Figure 6, the $(Pb_2Cl_9)_n^{-5}$ chain is formed from $PbCl_6$ octahedra by alternate sharing of vertices and edges. There are two independent Pb(II) atoms, with mean Pb-Cl distances of 288.8 and 289.8 pm, respectively.

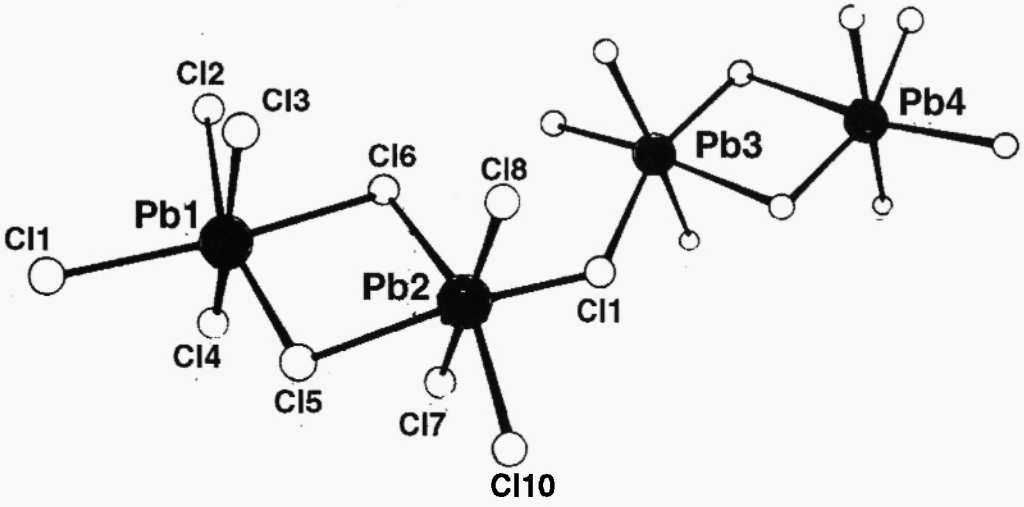

Fig.6. View of $[Pb_2Cl_9]_n^{-5}$ [106]

In another complex anion $[Pb_4Cl_{11}]^{-3}$ [108] two crystallographically independent Pb(II) atoms are present and show distorted trigonal prismatic coordination by chlorine atoms, with one additional chlorine atom above one of the rectangular faces of the prism. The prisms share corners thereby forming a three dimensional network held together by $[Co(NH_3)_6]^{+3}$ cations.

In $[PbCl_6]^{-2}$ anion [109], the Pb(IV) atom is surrounded by six chlorine atoms and form an almost regular arrangement about the metal atom. There are three derivatives [110-112] which contain the complex anion $[PbBr_4]^{2}$ with each Pb(II) atom is six coordinate with a mean Pb-Pb distance of 302 pm.

In $[Pb_2Br_5]^{-}$ [113] each Pb(II) atom has two close bromine neighbours at 289 pm, with the next nearest bromine ions at 316 pm in the vertical rows. The next four bromine neighbours at 335 pm are all closely attached to other lead atoms.

There are five derivatives of the formula $L^{+}[PbI_3]^{-}$ where the cation is a bulky organic moiety, NMe_4^{+} [114], piperidinium [115], quinolinium [116], tetramethylethylenediamineH [117] or hexamethylenetetra-amineH [118], all of which are isostructural. The structure consists of PbI_3 chain units running along the c axis. The $[PbI_3]_n^{-n}$ chain is formed by face-shared PI_6 octahedra. The organic cations sit in holes in the packing of the iodide ions. The mean Pb-I distance in this series is 322.7 pm, and the shortest Pb-Pb separation ranges from 383.5 pm to 406.3 pm. There is a correspondence between the Pb-Pb separation and the Pb-I-Pb bond angles. As the latter opens the former decreases, for example: 72.8(1)° and 383.5(1) pm [118], 75.76(1)° and 395.8(1) pm [114], 78.0(1)° and 406.3(1) pm [115].

Infinite $[PbI_3]_n^{-n}$ anion chains have also been observed in $APbI_3.nH_2O$ (A = NH_4^{+}, K, Rb or Sc; n = O or 2) [119-121]. The structures contain $[PbI_3]^{-}$ double chains of edge-sharing PbI_6 octahedra. The chains extend along *b* and are connected by A and H_2O molecules. The difference in the structure between two types of $[PbI_3]_n^{-n}$ chains in $LPbI_3$ [114-118] and $APbI_3$ [119-121] might be a result of the size of the positively charged moiety in the system [118]. The mean Pb-I distance of 323.7 pm and mean Pb-Pb separation of 471 pm found in the latter series is longer than the values of 322.7 pm and 397 pm of the former.

There are two orange derivatives $(L^{+})_2[PbI_4]^{-2}$, where L is phenethylammonium [123] or n-nonylammonium [124] in which the Pb(II) atoms are octahedrally coordinated by six iodine atoms. The octahedra are joined by their corners to form an infinite two dimensional polyanionic network parallel to the *ab* face of the crystal. The nets are separated by L^{+} cations extending throughout the crystal. While the mean Pb-I distance of 319 pm is only about 4 pm shorter than that of 323 pm found for the $[PbI_3]^{-}$ derivatives, the Pb-Pb separation of 627.4(1) pm [124] is much longer than those found in the series of $LPbI_3$ (397 pm) [114-118] and in $APbI_3$ (471 pm) [119-121]. The value for one of the derivatives [123] is not given.

The structure of yellow $[H_2NC(I)NH_2]_3[PbI_5]$ [125] is configured in a manner such that iodoformamidium cation layers terminate the three dimensional cubic perovskite structure along the [110] direction, resulting in a single [110]-oriented $[H_2NC(I)NH_2]PbI_3$ perovskite sheets. These are actually characterised by infinite, corner sharing, one dimensional PbI_5 octahedra chains held together by organic cations. The Pb-I distances range from 315.3(3) to 328.7(3) pm, mean value 321.5 pm. The structure of orange $(Ph(CH_2)_2NH_3)(MeNH_3)[Pb_2I_7]$ [123] confirms the "bilayer" perovskite type in which each Pb(II) atom is six coordinate (PbI_6) with the mean Pb-I distance of 317.7(3) pm.

The crystal structure of black "iodide of Wells", $K_3Pb_2I_8.4H_2O$ [126], is divided into an ordered part $K_2PbI_4.2H_2O$, and a disordered part $0.237KI_3.0.37H_2O$. The former is an unexpectedly simple arrangement of linear chains along the (001) plane of edge bridged octahedrally coordinated anionic complex $[PbI_{4/2}I_2]^{-2}$ anions, K^{+} cations and water molecules, leaving two different channels parallel to the chains. This is caused by filling one channel entirely with a one dimensional tri-iodide chain (I_3^{-}), which is incommensurate with the transition of the former part. The other is partially filled with K^{+} and H_2O. The Pb-I distances are 323.5(1) pm (x4) and 321.4(1) (x2).

Inspection of the data for homo-lead halides in Table 3 shows only four Pb(IV) derivatives [109], each of them having almost regular octahedral coordination utilizing six chlorine atoms. The mean Pb(IV)-Cl bond distance is 245 pm. The more plentiful Pb(II) examples are found in coordination with all of the halogen atoms and with coordination numbers from five to nine. The coordination number is seen to decrease with increasing radii of the halide ligand atoms, for example: F (58 pm) nine coordinate only; Cl (99 pm) from five to nine; Br (119 pm) six and eight only; I (133 pm) six coordinate only. The Pb-X distance also increases with coordination number and the covalent radius of the X atom, for example: Pb-Cl (mean) 287.6 pm (six-) < 298 pm (seven-) < 305 pm (eight-) < 313 pm (nine-); Pb-Br 302 pm (six-) < 320 pm (eight). The mean Pb-X distances for six coordinate complexes increase in the sequence: 287.6 pm (Cl) < 302 pm (Br) < 321.6 pm (I). For nine coordinate the sequence is: 265 pm (F) < 313 pm (Cl). The Pb-X distance reflects the oxidation state of the lead atom, for example: Pb-Cl for $PbCl_6$ 265 pm for Pb(IV) < 287.6 pm for Pb(II).

It is noticed that the mean Pb-Pb separation decreases with the covalent radii of X in the order: 422 pm (Cl) < 403 pm (Br) < 393 pm (I). Unfortunately for PbX_9 the data are not available in the original papers. The shortest Pb-Pb bond distance found in the deries of Pb(II) halides is 374(5) pm

[113] and the longest is 627.4 pm [124]. However, there are again examples for which data are not available.

In addition to the homohalides, many mixed halides have also been characterised by X-ray analysis and are summarised in Table 3. The following compositions are found: PbFCl; PbClBr; PbClI; PbBrI; $6PbF_2.PbCl_2$; $4PbF_2.PbI_2$. $5PbF_2.PbBr_2$; $5PbF_2.PbI_2$; $7PbF_2.PbI_2$; and $Na_2Pb_{11}F_{18}Br_6$.

The structure of colourless tetragonal PbFCl [127,128] contains Pb(II) atoms which are surrounded by both fluorine and chlorine atoms. There are four fluorine atoms at a distance of 255 pm, four chlorine atoms at 308 pm, and an additional chlorine atom at 320 pm to complete the nine coordinate PbF_4Cl_5 environment. The Pb-Pb separations are 409, 414 and 514 pm. The complex PbFCl has an important tetragonal layer lattice structure type frequently adopted by large cations in the presence of two anions of differing size [134].

In the infinite columns of $6PbF_2.PbCl_2$ [129] are three different sites for the lead atoms in the space group P6, such as Pb(1) in 1(b) with point symmetry 6; Pb(2) in 3(k) and Pb(3) in 3(j) with point symmetry m in each. The coordination polyhedra are: Pb(1), a triple capped trigonal prism formed by nine fluorine atoms; Pb(2), a square archimedian antiprism formed by six fluorine and two chlorine atoms, plus a fluorine outside the larger square which involves the chlorine atoms; Pb(3), a deformed triple capped trigonal prism formed by seven fluorine and two chlorine atoms.

The structures of the compounds, $5PbF_2.PbBr_2$ and $nPbF_2.PbI_2$ (n = 4,5 or 7) [130] are built up from Pb(II) layers and X^- layers. The layers are either close-packed as in the trigonal or pseudo-trigonal structures, $4PbF_2.PbI_2$ and $5PbX_2.PbX_2$ (X = Br or I), or have body-centred cubic packing as in the pseudo-tetragonal structure of $7PbF_2.PbI_2$. Subsequent layers of Pb(II) in the structures may be summarised as "PbF_2" blocks. In total, the "PbF_2" blocks in a unit cell contain as many interstitial F^- ions as there are X^- ions in the same cell. Blocks including 2,3 or 4 Pb(II) layers have hitherto been found. The shortest Pb-Pb separations are: 381(1) pm in $4PbF_2.PbI_2$; 391.1(3) in $7PbF_2.PbI_2$; 403.0(4) pm in $5PbF_2.PbBr_2$, and 404.2(2) pm in $5PbF_2.PbI_2$ [130]. The Pb-X distances are given in Table 3.

The asymmetric part of the unit cell of $Na_2Pb_{11}F_{18}Br_6$ [131] contains two Pb(II) atoms in 6(h) positions. One of them is eight coordinated by four fluorine (mean Pb-F = 244.9 pm) and four bromine (mean Pb-Br = 324.6 pm) atoms. The other is nine coordinated by seven fluorine(mean Pb-F = 258.5 pm) and two bromine (mean Pb-Br = 339.0 pm) atoms. The mean Pb-Pb separation is 397.3(1) pm.

There are three mixed halides of the composition PbClX (X = Br or I) and PbBrI [132,133], and the structure of PbBrI is shown in Figure 7. The Pb(II) atoms have eight or nine neighbouring X atoms. There is a wide range of Pb-X distances between any particular pair of ions, showing that the arrangement of halogen ions departs considerably from a close-packed array.

In the series of Pb(II) mixed halides one can find Pb(II) atoms with from eight to eleven X atoms. The most common halide is fluorine. There is a wide range of distances between any particular pair of halides. The mean Pb-X distance increases with the covalent radius of the respective X atom in the sequence: 260 pm (range 218-305 pm) (F) < 308 pm (range 291-333 pm) (Cl) < 324 pm (298-355 pm) (Br) < 350 pm (317.5-384 pm) (I). The Pb-Pb separation increases with decreasing covalent radius of the radius of X, as in the homo-halide series, for example: 392 pm (F+I) < 400 pm (F+Br) < 445 pm (F+Cl).

5. HETEROMETALLIC LEAD HALIDES

Structural data for almost forty heterometallic lead halides are summarised in Table 4. In colourless α-$SnPbF_4$ [135] the cationic framework is composed of layers perpendicular to the *c* axis in the sequence Pb-Pb-Sn-Sn. The fluorine atoms occupy two types of position, the normal and the interstitial. The coordination about Sn(II) consists of ten fluorine atoms with a mean Sn-F distance of 237 pm. The Pb(II) atom is eight coordinated by fluorine with a mean Pb-F distance of 264 pm.

In another colourless derivative [136], two independent Pb(II) atoms are present, each with nine neighbour atoms giving chromophores of PbF_6O_3 and PbF_5O_4.

Their are twelve fluorine atoms around Pb(II) in the pale yellow compound $PbPtF_6$ [137] in two sets with Pb-F distances of 257 and 298 pm. The Pt(IV) atom is six coordinated to fluorine atoms with a mean Pt-F distance of 190 pm.

In $PbZrF_6$ [138] the ZrF_8 dodecahedra connect by an edge to form chains parallel to the *ox* axis chains. The Pb(II) atoms are intercalated between the chains, with ten fluorine

TABLE 4. Crystallographic and Structural Data for Heterometallic Lead Halides[a]

COMPOUND (colour)	Cryscl Sp.Grp Z	a[pm] b[pm] c[pm]	α [°] ß [°] γ [°]	Chromo phore	M-L [pm]	M-M [pm] M-L-M [°]	L-M-L [°]	Ref
α-$SnPbF_4$	m			$Pb^{II}F_8$	F[b] 254(2) x4		F,F[b] 64.9-111.7(2)	135
	P2/n				274(4,3)		174.3(2,8)	
(colourless)	?				(ave. 264)			
				$Sn^{II}F_{10}$	F 198-263(6)		F,F 59.4-127.7(12)	
					(ave. 237		168.9(10,3)	
$PbSiF_6.4H_2O$	m	784.4(1)		$Pb^{II}F_6O_3$	F 255.6-281.9(11)		not given	136
	$P2_1/c$	799.6(2)	91.55(1)		(ave. 269.1)			
(colourless)		1264.9(3)			O 252(1,17)			
				$Pb^{II}F_5O_4$	F 258.1-279.3(9)			
					(ave. 268.9)			
					O 239.5(10,14)			
					282.9(13,29)			
				$Si^{IV}F_6$	F 168.8(12,24)		F,F 90.0(6,2.4)	
							177.5(6,1.0)	
$PbPtF_5$	hx	722.7		$Pb^{II}F_{12}$	F 257 x6			137
					298 x6			
(pale yellow)		707.1		$Pt^{IV}F_5$	F 190			
$PbZrF_6$	or	754.9(4)		$Pb^{II}F_{10}$	F 256 x4	378[c]	F,F 33.29-55.07	138
	Cmma	1112.3(6)			274 x4			
(pale yellow)	4	531.0(3)			269 x2		F,F 61.02-99.04	
				$Zr^{IV}F_8$	F 219(-,1)	377[d]		
Pb_3RhF_7	m	556.9		$Pb^{II}F_8$	F 237.5-390.9[c]	390.9[c]		139
	$P2_1/c$	1185.4	91.0	(F_{2-3})	295.7-408.0[c]	408.0[c]		
	4	883.2			(ave. 259-453.8[c]	453.8[c]		
					(F) 337(-,37)			
				$Rh^{III}F_6$	F 197.0(20,46)	351.6[e]	F,F 90.0(-,11.4)	
						368.0[e]	176.1(-,1.6)	
Pb_3ZrF_{10}	or	1071.3(3)		$Pb^{II}F_8$	F 250(1) x4			140
	Cmcm	1281.7(4)			266(3) x4			
	4	590.9(2)		$Pb^{II}F_{11}$	F 253-304(4)			
					(ave. 274)			
				$Zr^{IV}F_8$	F 210(4,7)			

$Pb_2Al_2F_{12}$	m	943.5(6)			$Pb^{II}F_3$	F	228-301(2)	398-545(1)[c]				141
	$P2_1/n$	961.0(5)	90.59(5)		(F_5)		(ave. 264)					
(colourless)	4	1010.0(9)				(F)	331(-,34)					
					$Al^{III}F_6$	F	180(2,5)		F,F	90.0(1,0,3.4)		
										175.9(9,3.0)		
$Pb_3Fe_4F_{12}$	tr	740.3(2)	110.45(2)		$Pb^{II}F_3$	F	232-301(2)	391-467(1)[f]				142
	P$\bar{1}$	762.1(2)	107.98(1)		(F_{4-5})		(ave. 262.5)					
(colourless)	2	989.0(3)	95.92(2)			(F)	342(2,33)					
					$Fe^{III}F_6$	F	193(2,6)		F,F	90.0(1.0,12.8)		
										172.4(7,6.8)		
$Pb_5Al_3F_{19}$	tg	2017.38(4)			$Pb^{II}F_9$	F	229-305(4)					143
	P4/m				x4		(ave. 269)					
(colourless)	8	722.05(1)			$Pb^{II}F_{10}$	F	225-304(4)					
							(ave. 266)					
					$Al^{III}F_6$	F	180(4,11)					
$Pb_5Cr_3F_{19}$	tg	1438.4(5)			$Pb^{II}F_9$	F	235.7-293.2(18)					144
	I4cm				x4		(ave. 269)					
(deep green)	4	740.8(2)			PbF^{-1}_{10}	F	226.7-302.5(10)					
							(ave. 266)					
					$Cr^{III}F_5$	F	189(2,6)					
KPbLaF$_5$	tg	654.4(1)			MF_3	F	250.0(12) x6					145
	P3				(Pb,La)		253.6(19) x3					
	1	380.40(9)										
					MF_3	F	258.9(12) x6					
					(Pb,La)		249.3(26) x3					
					KF_9	F	299.9(16) x6					
							253.0(34) x3					
$KPbCr_2F_9$	or	981(5)			$Pb^{II}F_9$	F	239.8-283.1(7)					146
	Pnma	541.2(3)					(ave. 265.6)					
(light green)		1393(1)			$Cr^{III}F_5$	F	189.9(7,28)	-	F,F	90.0(-,5.5)		
								155.7(-,3.3)[d]		176.9(-,6.2)		
					KF_9	F	269.3-298.7(7)					
							(ave. 287.3)					
$NaPbFe_2F_9$	m	730.8(3)			$Pb^{II}F_{10}$	F	258-299(1)		F,F	92.9(8,5.2)		147
	C2/c	1255.9(5)	93.06(2)				(ave. 276)					
	4	764.0(3)			$Fe^{III}F_5$	F	184-199	-				
							(ave. 191)	134(1)[d]				
								159(1)[d]				
					NaF_9	F	253(1,24)					

$Pb_2MnFe_2F_{12}$	hx	932.0(1)		$Pb^{IV}F_4O_2$	F	258.7(3,0)	412.7(1)[e]	F,F	90.6(3,4.9)	148
	P62m				H_2O	282.4(2,0)			117.4(3)	
$.3H_2O$	1	396.18(5)		MF_6 (Mn^{II}, Fe^{III})	F	198.2(3,27)	391.9(1,43)[d] 149.4(1)[d] 179.5(1)[d]		179.5(1)	
(light brown)										
$Na_3Pb_2(BeF_4)_3F$	hx	953.1(3)		$Pb^{II}F_7$	F	238.5-178.8(4) (ave. 253.2)		F,F	55.7-120.2(6) 148.3(3,2.5)	149
	$P6_3/m$									
	2	702.8(2)		$Be^{II}F_4$	F	153.1(9,15)		F,F	109.4(5,6.0)	
				NaF_2	F	240.9(4) x3 250.2(5) x3 287.9(5) x3		F,F	54.7-115.9(1)	
$BaPbF_5$	hx	745		$Pb^{IV}F_5$	F	204				150
	R3m									
	1	752								
$SrPbF_5$	hx	521		$Pb^{IV}F_6$	F	224				150
	$P4_2/mmc$									
	1	448		$Sr^{II}F_{10}$	F	260 x8 266 x2				
$MgPbF_5$	hx	525		$Pb^{IV}F_5$	F	198; 199				151
	R3									
		1396		$Mg^{II}F_5$	F	198; 199				
$ZrPbF_5$	hx	521		$Pb^{IV}F_6$	F	197; 198				151
	R3									
		1415		$Zn^{II}F_5$	F	198; 201				
$CdPbF_5$	hx	536		$Pb^{IV}F_6$	F	214				151
	R3									
		1509		$Cd^{II}F_5$	F	211				
$HgPbF_5$	hx	527		$Pb^{IV}F_6$	F	220				151
	R3									
		1590		$Hg^{II}F_6$	F	215				
$NiPbF_5$	hx	521		$Pb^{IV}F_5$	F	198; 199				151
	R3									
		1396		$Ni^{II}F_5$	F	200; 207				
$TlPb_2Cl_5$	m	895.4		$Pb^{II}Cl_x$	Cl	290-319				103
	$P2_1/c$	792.0	90.0							
	4	1248.7								

Tl_3PbCl_5	tg	844.8	$Pb^{II}Cl_7$	Cl 277.0-335.0(34)	383.8[e]	not given		152
	$P4_1$		(Cl)	(ave. 311)				
	4	1491.2		(Cl) 387.5(29)				
			$Tl^{I}Cl_7$	Cl 301.5-354.4(34)	383.4[d]			
			(Cl)	(ave. 323)				
				(Cl) 389				
Tl_3PbBr_5	or	1539.9	$Pb^{II}Br_7$	Br 288.5-332.3	441.6[e]	not given		153
	$P2_12_12_1$	906.3		(ave. 314)				
(colourless)	16	853.2	$Tl^{I}Br_8$	Br 321.2-371.5				
			(x2)	(ave. 344)				
			$Tl^{I}Br_7$	Br 327.9-355.3	363.0[d]			
				(ave. 336)				
Tl_3PbBr_5	tg	890.3	$Pb^{II}Br_7$	Br 306-350	395[e]			154
	$P4_1$			(ave. 330)				
(colourless)	4	1548.6	$Tl^{I}Br_7$	Br 309-376	404[d]			
				(ave. 337)				
$PbMo_3Cl_{14}$	c —	1292.1(1)	$Pb^{II}Cl_6$	Cl 287.6(3,0)				155
	Pn3							
(yellow-green)	4		$Mo^{II}Cl_6$	Cl 245.3(3,13)	260.0(2,3)[d]			
					367.8(3)[d]			
$PbMo_3Br_{14}$	c —	1350.4(2)	$Pb^{II}Br_6$	Br 299.5(3,0)				155
	Pn3							
(yellow-orange)	4		$Mo^{II}Br_6$	Br 259.3(3,23)	262.1(2,7)[d]			
					370.7(3)[d]			
$PbMo_3I_{14}$	c —	1442.9(2)	$Pb^{II}I_6$	I 320.4(2,0)				155
	Pn3							
(ruby red)	4		$Mo^{II}I_6$	I 278.6(2,72)	267.3(3,1)[d]			
					377.9(3)[d]			
$TlPbI_3$	or	462.5(2)	$Pb^{II}I_6$	I 318.1(1,0)	-		I,I 90.0(1,2.7)	156
	Cmcm	1488.5(4)		322.0(1,0)	91.81(3)[c]		180.00(3,0)	
(red)	4	1185.7(4)			137.43(3)[c]			
					95.9(-,9.8)[e]			
			$Tl^{I}I_8$	I 346.7(1) x2	-		I,I 64.77-140.22(1)	
				361.4(1) x4	151.57(1)[e]			
				397.1(1) x2	81.6(-,2.0)[d]			
					113.97(2)[d]			
Tl_4PbI_6	or	1911.7(9)	$Pb^{II}I_6$	I 318.7(2) x2	-		I,I 90.0(1,2.6)	156
	Pbam	987.7(9)		323.4(2) x4	90.15(3)[c]		180.00(4)	
(orange)	2	458.6(4)			95.9(-,6.8)[e]			
					138.0(-,3.6)[e]			

			Tl_7I_7	I	339.2-371.6(2) (ave. 354)	364.9(2)[d] 386.9(2)[d]	I,I 70.84-142.42(4) 166.89(1)	
			$Tl^{I}I_8$	I	340.5-388.5(3) (ave. 366)	- 60.51-153.15(3)[d]	I,I 69.42-148.05(2)	
Tl_6PbI_{10}	hx P62c	1056.1(4)	$Pb^{II}I_6$	I	311(1) x3 334(2) x3	306(2,5)[c] 375(2)[c]	I,I 61.0(3,0) 84.4-124.1(3) 174.9(5,0)	157
(black)	2	1352.1(6)						
			$Tl^{I}I_9$	I	340-393(2) (ave. 367)	431(1,13)[e] 657(1,25)[e]	I,I 50.9-148.4(3)	
β-$ThPbI_6$	hx P31c	778.1(6)	$Pb^{II}I_6$	I	319.7			158
	?	1384.4(14)	$Th^{IV}I_6$	I	306.7			
γ-$ThPbI_6$	or	438.7(1)	MI_8	I	313.4 x2			158
	Cmcm	1395.6(8)			328.9 x4			
	?	1000.5(7)			343.6 x2			
$SrPb_2I_6.7H_2O$	tg $I4_1/amd$	1177(2)	$Pb^{II}I_6$	I	314(4) x3 320(2) x3	- 140(2,1)[c]		159
(orange)	4	1732(2)	$Sr^{II}O_5H_2O$		245			

Footnotes:

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Pb-Pb distance, Pb-L-Pb angle.

d. M-M distance, M-L-M angle.

e. Pb-M distance, Pb-L-M angle.

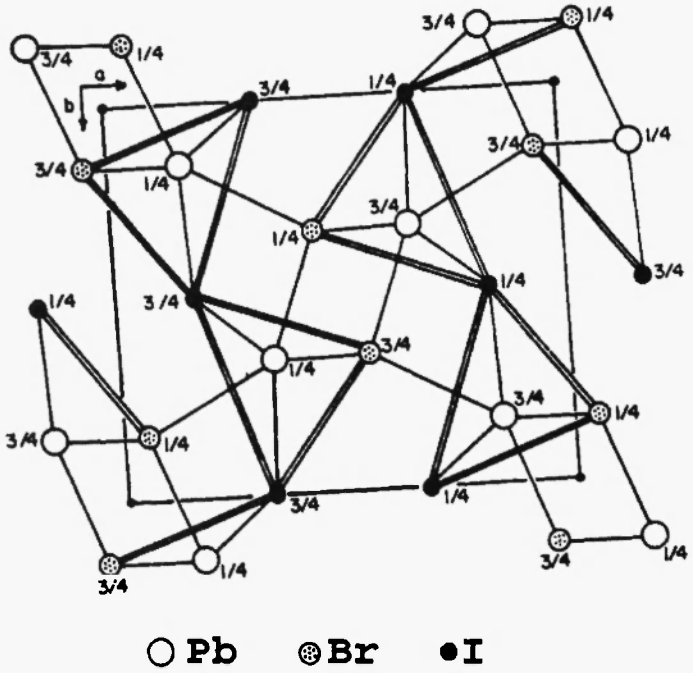

Fig.7. *c* Axis Projection of the PbBRI Structure [133]

atoms around each at a mean distance of 266 pm. The metal-metal separations are almost equal for Pb-Pb (378 pm) and Zr-Zr (377 pm).

In carmine red Pb_2RhF_7 [139] one fluorine atom is coordinated to three Pb(II) atoms only, while the other six fluorines form a distorted octahedron around ruthenium. In the polymer network the Pb-Rh distances of 351.6 and 368.0 pm are much shorter than the Pb-Pb distances of 390.9, 408.0 and 453.8 pm.

The structure of Pb_3ZrF_{10} [140] was described as an ordered intergrowth of $(Pb_2F_4)_n$ fluorite-like unidimensional units and a $(Pb_4Zr_2F_{16})_n$ columnar cluster consisting of two isolated square antiprisms sharing faces with four $[PbF_{11}]$ complex polyhedra.

The structure of colourless $Pb_3Al_2F_{12}$ [141] exhibits isolated $[Al_4F_{20}]^{-8}$ tetrameric groups of octahedra encaged in a subnetwork of Pb(II) polyhedra around "independent" fluoride ions. The two independent fluorine sites are tetrahedrally surrounded by four Pb(II) atoms. The corresponding $[FPb_4]$ tetrahedra are both irregular and elongated. Two tetrahedra, sharing the Pb(3)-Pb(3) edge, form bis-tetrahedral groups $[F_2Pb_6]$. These groups are corner connected by Pb(3) atoms and form infinite chains of alternating bis-tetrahedra along the corners, leading to a three dimensional subnetwork. It forms a cavity surrounded by twenty Pb(II) atoms where the tetrameric ring is encaged. Bond distances and angles are given in Table 4. The $Pb_3F_2F_{12}$ molecule [142] is isostructural with that of $Pb_3Al_2F_{12}$ [141].

There are two derivatives of the composition $Pb_5M_3F_{19}$ (M = Al(III) [143], or Cr(III) [144]) which are isostructural. The structure consists of connected PbF_9, PbF_{10} and MF_6 polyhedra that share corners, edges and faces. Nine coordinate (PbF_9) was discussed as a distorted tricapped trigonal antiprism. Ten coordinate (PbF_{10}) was described as bisdiphenoidal. The mean Pb-F distance in PbF_9 of 269 pm is about 3 pm shorter than that of PbF_{10} (mean 266 pm).

In $KPbLaF_6$ [143] all the metal atoms (K(I), Pb(II) and La(III)) are surrounded by nine fluorine atoms to form a polymeric network. In light green $KPbCr_2F_9$ [146] the $(CrF_6)^{-3}$ octahedra share common corners (in a *cis* position) and form zig-zag chains $(CrF_5)^{-2}$ parallel to the *b* axis. Two identical chains are linked together by common corners in the (101) plane, and thus form a double chain $(Cr_2F_9)_n^{-3n}$. The K(I) and Pb(II) atoms are between these chains and ensure the cohesion of the lattice. Three of the fluorine atoms are found in bridging positions in the chains, while the other three are in terminal positions.

The framework structure of $NaPbFe_2F_9$ [147] is formed by three dimensional corner sharing of octahedra (Fe). Infinite chains run parallel to the *c* axis (Fe(2) only) and along the (110) and 1$\bar{1}$0)

directions (alternating Fe(1) and Fe(2)). Bridging fluorines are always in a *trans* position. The PbF_{10} units form an approximate bicapped square antiprism.

The structure of hexagonal prismatic light brown $Pb_2MnFe_2F_{12}.3H_2O$ [148] contains three chains of MF_6 octahedra (M = Mn(II), Fe(III) statistically distributed at the same site) sharing trans corners along (001) and connected by *cis* corners to form a triple infinite isolated chain of formula $[M_3F_{12}]_n^{-4n}$. The Pb(II) atom is coordinated by a trigonal prism of F atoms tricapped by the water molecules.

The structure of $Na_3Pb_2[BeF_4]_3F$ [149] is of the apatite variety, the position 4f is occupied exclusively by Na(I), whereas four Pb(II) and two Na(I) atoms are distributed statistically in position 6h. The Be(II) atom is tetrahedrally coordinated by fluorine atoms with the mean Be-F distance of 153.1(9) pm. The Pb(II) is surrounded by seven fluorine atoms with the mean Be-F distance of 153.1(9) pm. The Pb(II) is surrounded by seven fluorine atoms in pentagonal bipyramidal arrangement with a mean Pb-F distance of 253.3(4) pm. The nine fluorine atoms about Na(I) form a tricapped trigonal prism (mean Na-F = 260 pm).

There are seven derivatives of composition $M^{II}PbF_6$ (M = Ba, Sr, Mg, Zn, Cd, Hg or Ni) [150,151] where the Pb(IV) atom is six coordinated with the mean Pb-F bond distance of 208 pm.

In colourless Tl_3PbX_5 (X = Cl [152] or Br [153,154]) the metal atoms are surrounded by seven X ions. These polyhedra are connected in a three dimensional way. The bromine derivatives exist in two isomeric forms, orthorhombic [153] and tetragonal [154].

There are three coloured derivatives of the composition $PbMo_6X_{14}$ (X = Cl, Br or I) [155] all have the structure shown in Figure 8. It consists of $\{[Mo_6X_8^i]X_6^a\}^{-2}$ groups with almost ideal octahedra of Mo_6. Each Mo(II) atom is surrounded by six X atoms. The mean Mo-X bond distance increases with the covalent radius of the halide: 245.3(3) pm (Cl) < 259.3(3) pm (Br) < 278.6(2) pm (I). The Mo-Mo bond distances follow this trend also: 260.0(2) pm (Cl) < 262.1(2) pm (Br) < 267.3(3) pm (I). The Pb(II) atoms are surrounded by six X atoms with a mean Pb-X distance which follows the trend of halide covalent radii: 287.6(3) pm (Cl) < 299.5(3) pm (Br) < 320.4(2) pm (I).

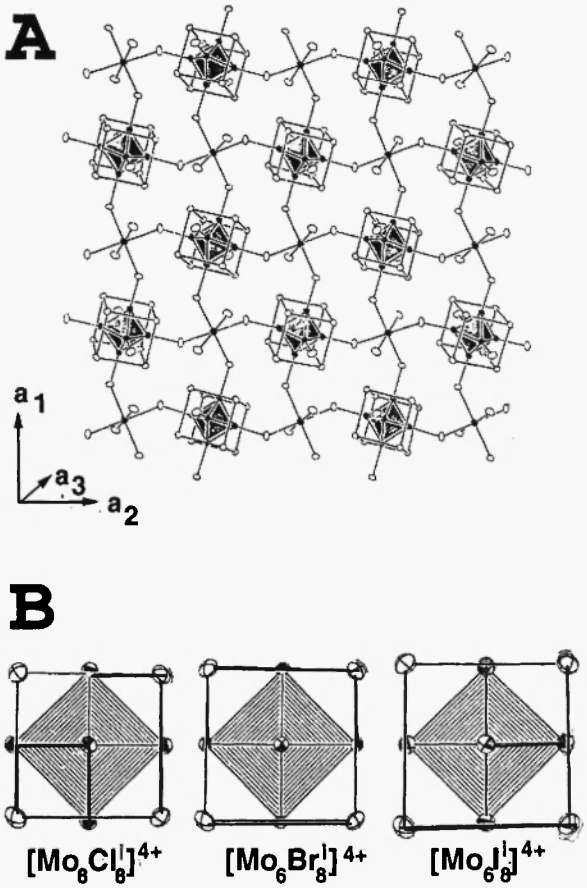

Fig.8. (A) Structure of $PbMo_6X_{14}$; (B) View of the $[Mo_6X_8]^{+4}$ Anion [155]

There are three coloured derivatives of composition $TlPbI_3$, Tl_4PbI_6 [156] and Tl_6PbI_{10} [157]. The black Tl_6PbI_6 unit [157] is built up by a framework of Tl_6I_6 with channels parallel to the *c* axes. The channels contain either Pb(II) or linear, nearly regular, I_4^{2} polyiodide ions. Each Pb(II) atom is surrounded by six iodine atoms. The Pb-Pb distance of 302(2) pm is the shortest found in the Pb(II) halide series.

Two isomeric forms are found for $ThPbI_6$ [158], differing by the number of coordinated iodine atoms about the metal atoms. In the b-form both Pb(II) and Th(IV) atoms are six coordinate with mean M-I distances of 319.7pm and 306.7 pm, respectively. In the g-form, eight iodine atoms form trigonal prisms about the metal atoms.

The structure of orange $SrPb_2I_6.7H_2O$ [159] is characterised by a three dimensional framework of octahedra [$PbI_{6/2}$] joined to one another through all the corners. The empty spaces of this framework are occupied by the Sr(II) atoms which are surrounded by six water molecules.

The data in Table 4 shows that of almost forty heterometallic lead halides only seven contain a Pb(IV) atom. In each case the Pb(IV) is six coordinated by fluorine atoms with a mean Pb(IV)-F bond distance of 208 pm (range 197-220 pm). The stereochemistry about Pb(II) varies from hexa- to dodecahedral. The mean Pb-X distance increases with coordination number as well as with covalent radius of the halide atom. For example, the mean Pb-F distances are in the sequence: 253 pm (seven-) < 261.5 pm (eight-) < 267 pm (nine-) < 268 pm (ten-) < 274 pm (eleven-coordinate). The mean Pb-X values for the six coordinate derivatives increase in the order: 288 pm (Cl) < 299.5 pm (Br) < 320 pm (I). For seven coordination the values are: 253 pm (F) < 311 (Cl) < 322 (Br). For eight coordination there are two values, 261.5 pm (F) and 329 pm (I).

In this series of heterometallics, lead is most commonly found with a six coordinate heterometal atom: M(II) = Sr, Ba, Mg, Zn, Cd, Hg, Ni, Mo and Mn; M(III) = Al,Rh, Cr and Fe; M(IV) = Si, Th and Pt. Three eight coordinate heterometal atoms are found: Na(I), Zr(IV) and La(III). Three nine coordinate heterometal atoms occur: Na(I), K(I) and La(III). The lowest coordination number of four was found about Be(II), and the highest of ten was found about Sn(II). The Pb-Pb distance of 302 pm [157] is the shortest found in Pb(II) halide chemistry. The Pb-Pb distance ranges from 302 to 545 pm. The shortest heterometal atom distance M-M is between two Mo(II) atoms at 259.8(2) pm [155], and the shortest Pb-M distance is 351.6 pm, where M is ruthenium [139].

6. CONCLUSIONS

This review summarises the published structures of over two hundred lead oxoacids and halides. Only fourteen of these have lead in an oxidation state of +4 [44,82,109,150,151], the remainder have lead in the oxidation state of +2. The coordination geometry about Pb(IV) is only octahedral, but the coordination geometry about Pb(II) varies from trigonal to dodecahedral, with square antiprism and, more commonly, eight coordinate tricapped trigonal prism predominating. The mean Pb^{IV}-X bond distance for octahedral derivatives increases with the covalent radius of the halide in the order: 208 pm (F) < 216 pm (OL) < 245 pm (Cl). These distances are shorter than those of the corresponding six coordinate Pb(II) bond: 256.5 pm (OL) < 288 pm (Cl), there being no $Pb^{II}F_6$ equivalent.

The mean Pb^{II}-X distances are summarised in Table 5. From the data one can see that the biggest variety of geometries about Pb(II) is built up with O-donor ligands. The variety of geometry in the Pb(II) halides decreases with increasing covalent radius of the respective halide atom. In general the mean Pb-X distance increases with coordination number and also covalent radius of the coordinated halide.

The shortest Pb-X bond distance found in the series of Pb(II) derivatives are: 218 pm (O); 237.5 pm (F); 277 pm (Cl); 288.5 pm (Br) and 311 pm (I). All are longer than the corresponding values for Pb(IV)-X which are: 207 pm (O); 197 pm (F) and 233 pm (Cl).

A summary of the metal-metal distances are given in Table 6, but the previously mentioned (Tables 1 to 4) missing data has left some gaps. The shortest Pb(II)-Pb(II) distance of 302 pm is about 42 pm longer than the value of 260 pm for Mo(II)-Mo(II) which is the shortest M-M distance for the heterometal lead compounds reviewed here.

There are examples, such as Pb(OH)Cl [43], Tl_3PbBr_3 [153,154] and $ThPbI_6$ [158], which exist in two isomeric forms. The $Cs_2PbCu(NO_2)_6$ structure was studied at different temperatures and found to be orthorhombic at 293K [55,56], monoclinic at 160K [57] and cubic at 420K [58]. There are two examples which exist in both anhydrous and hydrated forms: K_2PbBr_4 [111] and $K_2PbBr_4.H_2O$ [110]; $RbPbI_3$ [120] and $RbPbI_3.H_2O$ [119].

This review, together with its two precursors [2,3] represents the first overall survey of the structural data for lead derivatives and demonstrates the rich chemistry associated with lead. In some cases the relevant material is only available as supplementary data, and in other cases details

which are considered to be useful are missing, and this places limitations on comparative conclusions. The stereochemistry about the Pb(II) atom is often complicated by the presence of the lone pair of electrons in the valence shell of the lead. Complications also arise from differences of interpretation from author to author, such that distance over 260 pm are excluded from the inner coordination sphere by some, and distances up to 370 pm included by others. In this review the longer distances have been included in brackets in cases where the present authors have reconsidered the inclusion of these interactions in the inner coordination sphere (Tables 1 to 4).

Another limiting factor in this and earlier reviews has been the retrieval and location of a small percentage of the original publications. Retrieval problems are sometimes associated with choice of keywords, but location problems are increasingly due to the less tractable problem of fiscal restraint which has limited selection in many libraries. In this series of reviews on lead structures material was obtained from many sources, including local university libraries, the CISTI library at NSERC in Ottawa (Canada) and the British Patent's Office Libraries in London (England).

Table 5. Summary of the Mean Pb(II)-X Distances (pm) for Lead Inorganics

Coord. #	X = O	X = F	X = Cl	X = Br	X = I
3	236				
4	245				
5	256				
6	256.5		288	301	321
7	262.5	253	300	322	
8	272.5	261.5	305	321	329
9	274	266	313		
10	277	268			
11	282	274			
12	281	268.5			

Table 6. Summary of M-M Distances for Lead Inorganics

Pb-M	[pm]	M-M	[pm]
Pb-Pb	302 - 627	Fe-Ni	317
Pb-Li	322 - 398	Fe-Mn	387 - 396
Pb-Cu	332.5 - 337	Mo-Mo	260 - 378
Pb-Tl	384 - 441.6	Cu-Cu	283 - 354
Pb-Fe	392.5	Li-Li	300 - 320
Pb-Mn	412.7	Ni-Ni	315 - 322
Pb-K	421 - 451	Pt-Pt	326 - 330
Pb-Pt	549	Ag-Ag	338
		Tl-Tl	363 - 657
		Zr-Zr	377
		K-K	397 - 437
		Fe-Fe	785.5

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