Structural and Electrical Characterization of Polymeric Haloplumbate(II) Systems

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The synthesis and the structural, thermal, and electrical characterization of haloplumbate(II) systems are described. The counterions are diprotonated linear aliphatic amines, such as the 2-methylpentane-1,5-diamine (2meptH$_2$) and propane-1,3-diamine (pnH$_2$) dications. The (2meptH$_2$)[PbCl$_4$] and (2meptH$_2$)[PbBr$_4$] are isostructural, space group *Cc*, with $a = 24.140(4)$ Å, $b = 7.720(2)$ Å, $c = 7.795(2)$ Å, $\beta = 98.1(1)°$, $Z = 4$ for the chlorine compound and $a = 24.539(4)$ Å, $b = 8.031(2)$ Å, $c = 8.198(2)$ Å, $\beta = 99.6(1)°$, $Z = 4$ for the bromine compound; the (2meptH$_2$)[Pb$_{1.5}$I$_5$] crystallizes in the triclinic $P\bar{1}$ space group, with $a = 11.803(3)$ Å, $b = 12.565(3)$ Å, $c = 8.494(8)$ Å, $\alpha = 106.2(1)°$, $\beta = 100.5(1)°$, $\gamma = 117.4(1)°$, $Z = 2$; the crystals of (pnH$_2$)[PbCl$_4$] are orthorhombic, space group $P2_12_12_1$, $a = 19.247(4)$ Å, $b = 7.862(2)$ Å, $c = 7.581(2)$ Å, $Z = 4$; the (pnH$_2$)$_2$[Pb$_{1.5}$Br$_7$]·H$_2$O crystallizes in the triclinic $P\bar{1}$ space group, with $a = 11.517(3)$ Å, $b = 14.122(3)$ Å, $c = 8.149(2)$ Å, $\alpha = 104.1(1)°$, $\beta = 109.8(1)°$, $\gamma = 77.5(1)°$, $Z = 2$. Three different types of polymeric haloplumbate(II) systems were obtained: strictly monodimensional, (2meptH$_2$)[Pb$_{1.5}$I$_5$], ribbonlike, (pnH$_2$)$_2$[Pb$_{1.5}$Br$_7$]·H$_2$O, and perovskite-like structures, (pnH$_2$)[PbCl$_4$] and (2meptH$_2$)[PbX$_4$] (X = Cl, Br). Worthy of note is the presence of organic dications in their extended form, intercalated between the inorganic anions, which are at different distances, depending on the amine length. The nitrogen atoms of the ammonium cations interact with the inorganic anions forming a network of hydrogen bonds, which contribute to the crystal packing.

Introduction

The chemistry of transition metal complexes has been developed in recent years toward the construction of different/unusual structural model systems in order to rationalize the correlations between structures and physical properties.

Haloplumbates(II) represent a potential class of these materials because the flexibility of the Pb(II) coordination sphere and the nonstereospecific nature of the halide anions, modulated by the size and hydrogen-bonding properties of the cation, allow a large span of structural arrangements to be observable.[1,2] Thus, this system can be considered an ideal candidate for investigating the changing behavior from the low-dimensional inorganic lattice to the three-dimensional molecular network, due to the presence of intercalated organic cations.[3]

In a previous paper, in which saturated cyclic amines were employed as cations, we separated and investigated low-dimensional polymeric haloplumbate compounds.[4]

In this paper we report the synthesis and the structural, thermal, electrical, and spectroscopic characterization of mono- and bidimensional haloplumbate(II) systems of diprotonated amines, such as the propane-1,3-diamine and 2-methylpentane-1,5-diamine dication (hereafter abbreviated as pnH$_2$ and 2meptH$_2$, respectively) of formula XCH$_2$CH$_2$CH$_2$NH$_2$ (X = NH$_2$ (a), CH$_2$CH$_3$CHNH$_2$ (b)). (pnH$_2$)[PbCl$_4$], (pnH$_2$)$_2$[Pb$_{1.5}$Br$_7$]·H$_2$O, and (pnH$_2$)PbI$_4$ were prepared for the a series, while (2meptH$_2$)[PbX$_4$] (X = Cl, Br) and (2meptH$_2$)[Pb$_{1.5}$I$_5$] were obtained for the b series. The specific aim is to highlight the role of different diamine spacers which provide a flexible connection anchoring the inorganic systems, creating the opportunity to modulate the distances between the inorganic chains/layers.

Experimental Section

Synthesis. 2-Methylpentane-1,5-diammonium Tetrahaloplumbates(II). The crystalline compounds were precipitated by mixing concentrated hydrogen halide solutions (HCl (37%), HBr (40%), and HI (57%)) of the 2-methylpentane-1,5-diamine and PbX$_2$ (X = Cl, Br, I) in a 1:3 molar ratio and allowing the solutions to stand for several days at room temperature. By slow evaporation, white crystals (for the chloride and the bromide) and yellow crystals (for the iodide) were obtained. Elemental anal. Found for (2meptH$_2$)[PbCl$_4$] (compound **1**): C, 15.41; H, 3.95; N, 5.97. Calcd for C$_6$H$_{18}$PbCl$_4$N$_2$: C, 15.42; H, 3.88; N, 6.00. Found for (2meptH$_2$)[PbBr$_4$] (compound **2**): C, 11.18; H, 2.81; N, 4.30. Calcd for C$_6$H$_{18}$PbBr$_4$N$_2$: C, 11.17; H, 2.81; N, 4.34. Found for (2meptH$_2$)[Pb$_{1.5}$I$_5$] (compound **3**): C, 6.76; H, 1.73; N, 2.60. Calcd for C$_6$H$_{18}$N$_2$I$_5$Pb$_{1.5}$: C, 6.78; H, 1.71; N, 2.63.

Propane-1,3-diammonium Tetrahaloplumbates(II). The compounds were obtained by mixing propane-1,3-diamine and PbX$_2$ (X = Cl, Br, I) (1:3 molar ratio) in concentrated hydrogen halide solutions (HCl (37%), HBr (40%), and HI (57%)) and by allowing the solutions to stand for some days. The corresponding iodide complex was separated in a microcrystalline form; attempts to separate iodide crystals suitable for X-ray single-crystal analysis failed. The precipitated crystals

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Table 1. Crystallographic Data for Compounds **1**−**5**

	1	**2**	**3**	**4**	**5**
empirical formula	$C_6H_{18}Cl_4N_2Pb$	$C_6H_{18}Br_4N_2Pb$	$C_6H_{18}I_5N_2Pb_{1.5}$	$C_3H_{12}Cl_4N_2Pb$	$C_6H_{26}Br_7N_4OPb_{1.5}$
fw	467.2	645	1063.5	425.2	1040.4
space group	*Cc* (No. 9)	*Cc* (No. 9)	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
a, Å	24.140(4)	24.539(4)	11.803(3)	19.247(4)	11.517(3)
b, Å	7.720(2)	8.031(2)	12.565(3)	7.862(2)	14.122(3)
c, Å	7.795(2)	8.198(2)	8.494(8)	7.581(2)	8.149(2)
α, deg	90	90	106.2(1)	90	104.1(1)
β, deg	98.1(1)	99.6(1)	100.5(1)	90	109.8(1)
γ, deg	90	90	117.4(1)	90	77.5
V, Å^3	1438.2(7)	1593.0(8)	1000.2(18)	1147.2(5)	1196.4(10)
Z	4	4	2	4	2
T, °C	20	20	20	20	20
λ, Å	0.710 688	0.710 688	0.710 688	0.710 688	0.710 688
ρ_{obsd}, g cm^{-3}	2.12	2.62	2.49	2.44	2.85
ρ_{calc}, g cm^{-3}	2.16	2.69	3.53	2.46	2.89
μ, cm^{-1}	124.4	206.0	203.2	155.8	222.4
R^a	0.041	0.045	0.046	0.039	0.049
$R_w{}^b$	0.045	0.047	0.047	0.039	0.050

[a] $R = \sum|\Delta F|/\sum|F_o|$. [b] $R_w = [\sum w(\Delta F^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

are white (the chloride and the bromide) and yellow (the iodide) and are stable in air at room temperature. Elemental anal. Found for $(pnH_2)[PbCl_4]$ (compound **4**): C, 8.47; H, 2.90; N, 6.54. Calcd for $C_3H_{12}PbCl_4N_2$: C, 8.47; H, 2.85; N, 6.59. Found for $(pnH_2)_2[Pb_{1.5}Br_7]\cdot H_2O$ (compound **5**): C, 6.97; H, 2.50; N, 5.38. Calcd for $C_6H_{26}N_4OBr_7Pb_{1.5}$: C, 6.93; H, 2.52; N, 5.38. Found for $(pnH_2)[PbI_4]$ (compound **6**): C, 4.51; H, 1.60; N, 3.49. Calcd for $C_3H_{12}N_2I_4Pb$: C, 4.55; H, 1.53; N, 3.54.

Physical Measurements. Thermogravimetric and differential scanning calorimetric analysis were performed with a TA instrument DSC10 system equipped with a mechanical cooler and an automatic data acquisition and computer system TA 2000. Carbon, hydrogen, and nitrogen were analyzed with a Carlo Erba model 1106 elemental analyzer.

Single-Crystal X-ray Diffraction Studies. Important crystal parameters and refinement results are given in Table 1 for all of the compounds studied. X-ray data were collected using graphite-monochromatized Mo Kα radiation. The stability of the crystals was checked by measuring standard reflections during data collection; however, no significant loss of intensity was noted for any crystals. Corrections for Lorentz and polarization effects were always applied to the data. Additional information on data collection and structure solution and refinement is summarized below.

Data for **1**, **3**, and **4** were obtained on a Siemens AED diffractometer in the 2θ range of 6−56°. In this way 2370 (**1**), 4827 (**3**), and 1749 (**4**) unique total data were collected of which 1414 (**1**), 3028 (**3**), and 958-(**4**) having $I > 2\sigma(I)$ were considered as observed. Correction for adsorption was also applied following Walker and Stuart's method.[5] Data for **2** were collected on a Philips PW1100 diffractometer (2619 unique data, 1534 with $I > 2\sigma(I)$), while the crystals of **5** were mounted on a Enraf-Nonius CAD4 diffractometer (5778 unique data, 2616 with $I > 2\sigma(I)$). The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms are included in the final structure factors calculation in the calculated positions. All calculations were performed using SHELX86, SHELX76, PARST, and ABSORB programs.[6−9]

Complete details concerning data collection and refinements and final atomic coordinates are quoted in the Supporting Information. Selected bond distances and angles are listed in Tables 2−4.

Table 2. Bond Distances (Å) and Angles (deg) with Esd's in Parentheses Involving the Inorganic Moieties of Compounds **1**, **2**, and **4**

	1, X = Cl	**2**, X = Br	**4**, X = Cl
Pb−X(1)	2.870(12)	2.958(7)	2.850(6)
Pb−X(2)	2.892(12)	2.973(7)	2.895(6)
Pb−X(3)	2.817(14)	3.015(7)	2.822(6)
Pb−X(4)	2.875(15)	2.962(7)	2.848(7)
Pb−X(1)^i	2.846(12)	3.021(7)	2.871(6)
Pb−X(4)^{ii}	2.843(13)	3.023(7)	2.875(7)
X(1)−Pb−X(2)	90.4(4)	92.2(2)	91.2(2)
X(1)−Pb−X(3)	87.3(5)	88.5(2)	88.6(2)
X(1)−Pb−X(4)	91.9(4)	91.3(2)	86.5(2)
X(1)−Pb−X(1)^i	89.8(3)	89.8(2)	93.2(2)
X(1)−Pb−X(41)	177.5(4)	178.1(2)	178.1(2)
X(2)−Pb−X(3)	177.3(4)	179.3(2)	179.8(2)
X(2)−Pb−X(4)	91.0(4)	88.7(2)	88.2(2)
X(2)−Pb−X(1)^i	87.1(4)	89.6(2)	92.3(2)
X(2)−Pb−X(4)^{ii}	87.3(4)	86.2(2)	90.7(2)
X(3)−Pb−X(4)	90.5(4)	91.4(2)	91.7(2)
X(3)−Pb−X(1)^i	91.5(4)	90.3(2)	87.9(2)
X(3)−Pb−X(4)^{ii}	95.0(5)	93.1(2)	89.5(2)
X(4)−Pb−X(1)^i	177.5(4)	178.1(2)	179.5(2)
X(4)−Pb−X(4)^{ii}	88.8(4)	89.8(2)	93.9(2)
X(1)^i−Pb−X(4)^{ii}	89.4(4)	89.2(2)	86.4(2)
i	$x, 1-y, \frac{1}{2}+z$		$-x, y-\frac{1}{2}, -\frac{1}{2}-z$
ii	$x, 2-y, \frac{1}{2}+z$		$-x, y-\frac{1}{2}, \frac{1}{2}-z$

Table 3. Bond Distances (Å) and Angles (deg) with Esd's in Parentheses in the Inorganic Moiety of Compound **3**[a]

Pb(1)−I(2)	3.196(5)	Pb(2)−I(2)	3.290(3)
Pb(1)−I(3)	3.233(4)	Pb(2)−I(3)	3.287(5)
Pb(1)−I(4)	3.242(3)	Pb(2)−I(4)	3.346(4)
Pb(2)−I(1)	3.165(3)	Pb(2)−I(5)	3.109(4)
Pb(2)−I(1)^i	3.205(6)		
I(2)−Pb(1)−I(3)	85.9(1)	I(1)^i−Pb(2)−I(3)	172.8(1)
I(2)−Pb(1)−I(4)	88.7(1)	I(1)^i−Pb(2)−I(4)	97.2(1)
I(3)−Pb(1)−I(4)	85.9(1)	I(1)^i−Pb(2)−I(5)	96.7(1)
I(1)−Pb(2)−I(2)	87.2(1)	I(2)−Pb(2)−I(3)	83.5(1)
I(1)−Pb(2)−I(1)^i	91.2(1)	I(2)−Pb(2)−I(4)	85.4(1)
I(1)−Pb(2)−I(3)	87.4(1)	I(2)−Pb(2)−I(5)	173.9(1)
I(1)−Pb(2)−I(4)	168.7(1)	I(3)−Pb(2)−I(4)	83.4(1)
I(1)−Pb(2)−I(5)	92.7(1)	I(3)−Pb(2)−I(5)	90.4(1)
I(1)^i−Pb(2)−I(2)	89.4(1)	I(4)−Pb(2)−I(5)	93.8(1)

[a] $i = 1 - x, -y, -z$.

Electrical Measurements. Samples to be subjected to electrical and dielectrical measurements were formed into disks, up to 2 mm thick, by cold-pressing finely ground crystal powders under a pressure of 50 N/mm^2. A three-terminal electrode configuration, which has been

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Table 4. Bond Distances (Å) and Angles (deg) with Esd's in Parentheses in the Inorganic Moiety of Compound **5**[a]

Pb(1)−Br(1)	3.007(4)	Pb(2)−Br(4)	2.982(4)
Pb(1)−Br(2)	2.970(4)	Pb(2)−Br(5)	2.898(4)
Pb(1)−Br(3)	2.999(4)	Pb(2)−Br(6)	3.246(4)
Pb(2)−Br(1)	3.095(4)	Pb(2)−Br(7)	2.907(4)
Pb(2)−Br(2)^i	3.014(4)		
Br(1)−Pb(1)−Br(2)	89.6(1)	Br(2)^i−Pb(2)−Br(5)	88.0(1)
Br(1)−Pb(1)−Br(3)	91.7(1)	Br(2)^i−Pb(2)−Br(6)	84.8(1)
Br(2)−Pb(1)−Br(3)	86.4(1)	Br(2)^i−Pb(2)−Br(7)	92.8(1)
Br(1)−Pb(2)−Br(2)^i	85.3(1)	Br(4)−Pb(2)−Br(5)	95.2(1)
Br(1)−Pb(2)−Br(4)	90.4(1)	Br(4)−Pb(2)−Br(6)	91.5(1)
Br(1)−Pb(2)−Br(5)	88.1(1)	Br(4)−Pb(2)−Br(7)	91.7(1)
Br(1)−Pb(2)−Br(6)	84.8(1)	Br(5)−Pb(2)−Br(6)	170.3(1)
Br(1)−Pb(2)−Br(7)	176.9(1)	Br(5)−Pb(2)−Br(7)	89.5(1)
Br(2)^i−Pb(2)−Br(4)	174.5(1)	Br(6)−Pb(2)−Br(7)	97.4(1)

[a] $i = -x, -y, -z - 1$.

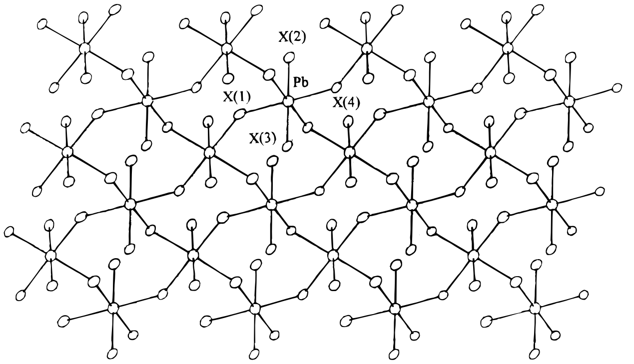

Figure 1. Perspective view of inorganic layers in the perovskite-like structures **1** and **4** (X = Cl) and **2** (X = Br) with vibrational ellipsoids at the 50% probability level.

proved to be the most suitable for these materials, was subsequently created on the surfaces by gold evaporation under vacuum. Samples were then sintered in a dry nitrogen atmosphere at 110 °C in order to eliminate moisture, minimize intergranular effects, and avoid decomposition of the material. Such a treatment could not applied to the $(pnH_2)[PbCl_4]\cdot H_2O$ compound. For this compound, to avoid water losses, measurements carried out on sintered, but anhydrous, samples turned out instead to be reproducible and have been reported. The voltmeter−ammeter method for direct current (dc) and a Schering bridge for alternating current (ac) measurements (2×10^{-1} to 1×10^5 Hz) were used with cells and instrumentation described elsewhere according to ASTM D257 and D150 standards, respectively.[10] Measurements were carried out in dry nitrogen to the highest allowable temperature which still provided reproducibility of measured values after cooling and subsequent heating. After measurements, samples were submitted to X-ray diffraction analysis to evaluate possible structural changes. As the pnH_2 iodide turned out to be extremely prone to decomposition after compression, electrical and dielectrical data are not reported.

Results and Discussion

As found in other halometalates, these compounds consist of inorganic anions and organic counterions. In general, three different types of polymeric haloplumbate(II) systems have been obtained: two-dimensional, layered structures, ribbonlike structures, and strictly monodimensional structures.

Perovskite-like Structure. Perovskite-like structure, shown schematically in Figure 1, is found in compounds **1**, **2**, and **4**, which are described below.

Crystal Structure of $(pnH_2)[PbCl_4]$. Compound 4. The structure consists of two-dimensional inorganic layers of $[PbCl_4{}^{2-}]_n$ anions and organic cations (Figure 2). In the inorganic layers, which lie in the *yz* plane, $PbCl_6$ corner-sharing octahedra are present, in which equatorial halogen atoms bridge four Pb atoms belonging to different octahedra, while the terminal ones are in the trans position with respect the equatorial plane. As shown in Table 2 of bond distances and angles, the octahedral geometry around the Pb is quite regular. The intra- and interlayer Pb⋯Pb distances, 5.45 and 9.678 Å, respectively, are similar to those found in haloplumbates presenting layered structure.[4]

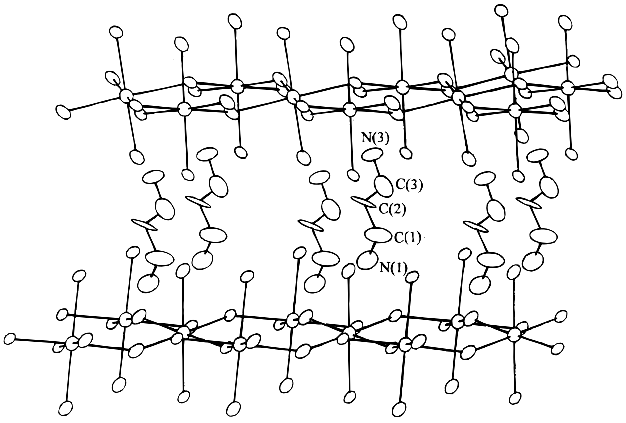

Figure 2. Perspective view of $(pnH_2)[PbCl_4]$ (**4**) with vibrational ellipsoids at the 50% probability level.

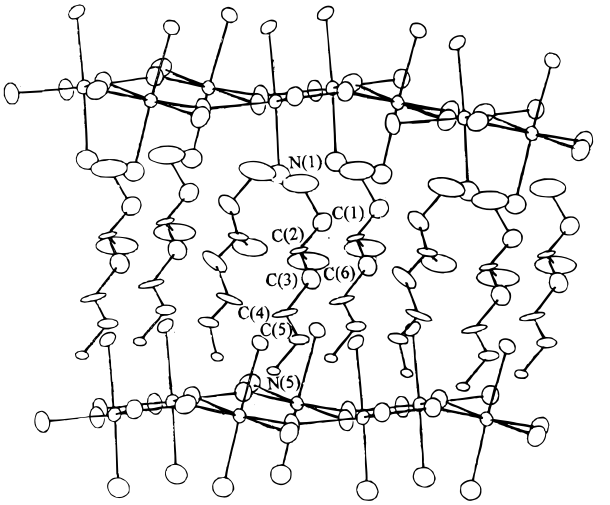

Figure 3. Perspective view of $(2meptH_2)[PbX_4]$ where X = Cl for **1** and X = Br for **2** with vibrational ellipsoids at the 50% probability level.

The diammonium cations, in the extended form, link adjacent layers via hydrogen bond interactions, involving both ends of each organic cation and terminal and bridging halide ions. The organic molecules are perpendicular to the two-dimensional layer anions, which are perfectly overlapped.

Crystal Structure of $(2meptH_2)[PbX_4]$ (X = Cl, Br). Compounds 1 and 2. The two methylpentanediamine complexes present a similar arrangement with respect to the above-described propanediammonium compound. The structure of both compounds consists of two-dimensional inorganic layers of $[PbX_4{}^{2-}]_n$ anions and organic cations (Figure 3 and Table 2).

In the inorganic layers, which lie in the *yz* plane, PbX_6 corner-sharing octahedra are present and equatorial halogen atoms X(1), X(4), X(1)′, and X(4)′ bridge four Pb atoms belonging to different octahedra, while the terminal ones, X(2) and X(3), are in the trans position with respect to the equatorial plane. As

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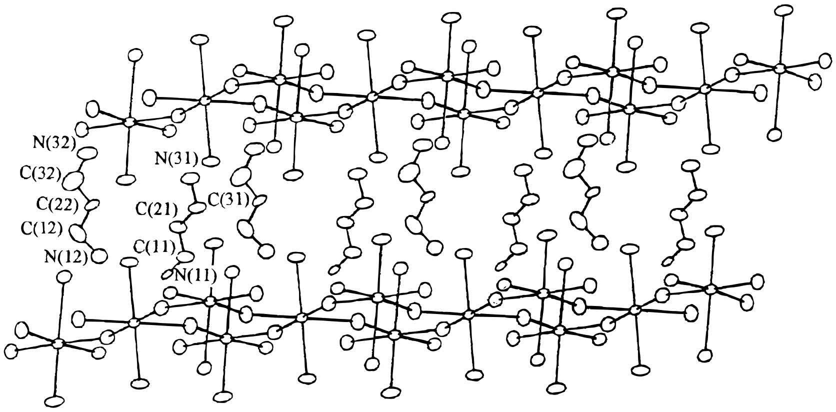

Figure 4. Projection of $(pnH_2)_2[Pb_{1.5}Br_7]\cdot H_2O$ (**5**) on the *xy* plane with vibrational ellipsoids at the 50% probability level. The water molecule is omitted for clarity.

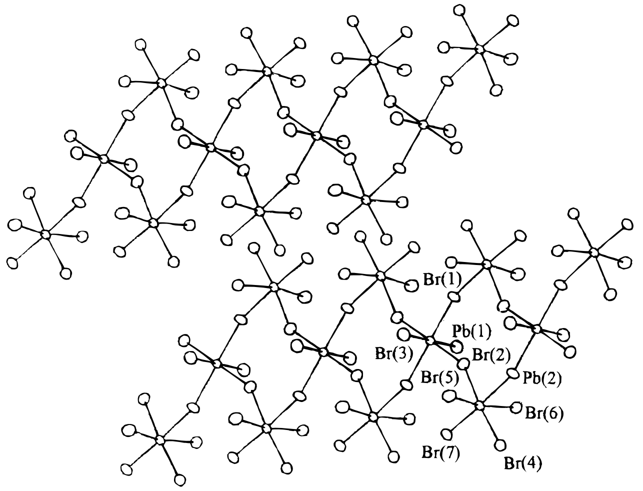

Figure 5. Perspective view of $(pnH_2)_2[Pb_{1.5}Br_7]\cdot H_2O$ (**5**), showing the ribbon arrangement with vibrational ellipsoids at the 50% probability level.

shown in Table 2, where bond distances and angles for both isostructural chlorine (**1**) and bromine (**2**) compounds are quoted, the octahedral geometry around the Pb is quite regular.

As expected, Pb−X bond distances increase monotonically from chloride to bromide, in keeping with the expected increase in halide radius. In these compounds there are two important differences which distinguish them from the above-considered compound: (a) the longer Pb···Pb interlayer distances, 12.15 and 12.7 Å respectively for chlorine and bromide compounds; (b) the ammonium cation and halide ions are not perfectly perpendicular and adjacent layers are not overlapped, but the Pb atoms belonging to two adjacent layers present a displacement of 18°. This is probably due to the strong steric effect of the CH_3 groups, directed toward the empty interlayer space, which determine not only a repulsive effect on adjacent ammonium dications but also a higher extension of the methylpentanediamine sheets.

Ribbonlike Structure. Crystal Structure of the $(pnH_2)_2[Pb_{1.5}Br_7]\cdot H_2O$. Compound 5. In this compound, organic dications, inorganic ribbons, and uncoordinated water molecules are present (Figures 4 and 5 and Table 4).

In the inorganic ribbons, running parallel to the *c* axis in the (110) plane, two crystallographically independent lead atoms, octahedrally surrounded by six halogen atoms, are present. The Pb(1), lying on the symmetry center at the origin of the cell, is connected to each Pb(2) by Br(1) and Br(2) bridging atoms.

Coordination around Pb(1) involves two terminal and four bridging bromine atoms, while around Pb(2) four terminal halogens are present. In this way, the inorganic ribbons are identified as tetranuclear centrosymmetric units running along the *c* axis.

In haloplumbate systems this ribbon structural archetype has never been observed till now.

The Pb(1) is octahedrally surrounded by two terminal [Br(3) and Br(3)′] atoms and four [Br(1), Br(2), Br(1)′, and Br(2)′] atoms bridging the Pb(2) atom. The long Pb(1)···Pb(2) distance (5.78 Å) is due to the presence of the bridging bromine atom giving rise to a nearly linear Pb(1)−Br(1)−Pb(2) (angle = 155.6(1)°) sequence. The Pb(2) atom is octahedrally surrounded by the two bridging [Br(1) and Br(2)] and four terminal bromine atoms [Br(4), Br(5), Br(6), and Br(7)]; this arrangement, which determines the ribbon formation, is probably due to the presence of uncoordinated water molecules which avoid the formation of the expected perovskite-like structural arrangements. The water molecules break the layers and link the ribbons through hydrogen-bond interactions with Br(4) and Br(7).

The Pb(1)···Pb(1) and Pb(2)···Pb(2) distances are 8.14 and 8.47 Å, respectively.

In the network, the polymeric ribbons are separated by about 12.61 Å in the (110) plane. Diammonium cations, in the extended form, link adjacent layers via hydrogen bond interactions, involving both ends of each organic cation and terminal halide ions in the same manner usually observed in perovskite-like compounds. Bond distances and angles in organic cation are similar to the values found in linear amines.

A network of strongly directional hydrogen-bonding interactions involving the protonated amine nitrogen atoms and the terminal coordinated bromine atoms completes the crystal packing.

Monodimensional Chain Inorganic Structure. Crystal Structure of $(2meptH_2)[Pb_{1.5}I_5]$. Compound 3. The structure consists of methylpentanediamine cations and infinite monodimensional polymeric chains, running along the *x* axis, in which trimeric $[Pb_3I_{10}{}^{4-}]_n$ units are connected by sharing edges (Figure 6 and Table 3), giving rise to an unusual arrangement for Pb(II) ions.

In the trimer, the Pb(1) atom, which lies on a symmetry center, is connected to two crystallographically independent Pb(2) metal atoms by three bridging atoms, I(2), I(3), and I(4). The six-coordination sphere of each Pb(2) is completed by a terminal I(5) atom and two symmetry-related atoms, I(1) and I(1)′, bridging two Pb(2) metal atoms which correspond to the top and the end of other adjacent trimers. Furthermore, a trans

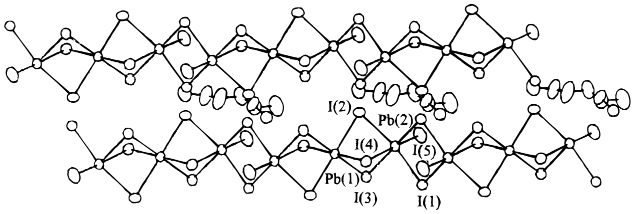

Figure 6. Perspective view of (2meptH$_2$)[Pb$_{1.5}$I$_5$] (**3**) with vibrational ellipsoids at the 50% probability level.

array of the terminal halogens, either inside or among Pb$_3$I$_{10}$ units, is observed. Each lead atom in the chain shows a distorted octahedral arrangement; in the trimer the octahedra share a triangular face via I(2), I(3), and I(4), while adjacent trimers are linked via Pb(2) octahedra sharing the I(1) and I(1)′ edges. The Pb···Pb contacts are different. In the trimeric inorganic unit the distance corresponding to the crystallographically independent atoms, Pb(1)···Pb(2), is 4.059(2) Å, shorter than the ones involving Pb atoms in adjacent trimers (PbX(2)···PbX(2) (1 − *x*, −*y*, −*z*), 4.457(5) Å).

As shown in Table 3, in the octahedra the Pb−I distances involving bridging iodine atoms range from 3.165(4) to 3.287(6) Å, in agreement with values found in Nagapetyan et al., and are greater than the ones involving the terminal iodine atom I(5) (3.109(4) Å).[1] The equatorial angles ranging from 85.9° to 94.1° for Pb(1) and 87.41 and 92.7° for Pb(2) indicate a slight distortion of the octahedra.

Bond distances and angles in organic cations are similar to the values found in linear amines.

In the network, the polymeric 1D endless inorganic chains run in the *x* direction, separated by 12.56 Å (*b* axis) and 8.49 Å (*c* axis) along the *y* and *z* directions, respectively. The extremely low and unusual distances among the chains along *z* directions are favored by organic cations, which lie almost parallel to the inorganic chains, connecting two adjacent inorganic chains through hydrogen-bonding interactions: N(5)···I(5) (1 + *x*, 1 + *y*, 1 + *z*) (3.54(2) Å), N(5)···I(5) (1 − *x*, −*y*, −*z*) (3.75(2) Å), N(1)···I(2) (−*x*, −*y*, 1 − *z*) (3.66(2) Å), and N(1)···I(3) (*x*, *y*, 1 + *z*) (3.73(2) Å). Also a van der Waals contact, involving terminal methyl groups of two centrosymmetrically related amines, is present: C(6)···C(6) (1 − *x*, 1 − *y*, 2 − *z*) (3.64(3) Å).

Thermal Behavior. The thermal behavior of the compounds was investigated by means of TG and DSC measurements. All the compounds do not present structural phase transitions, being stable from room temperature up to the melting point (275−300 °C), after which they decompose. At increasing temperature the anhydrous (2meptH$_2$)[Pb$_{1.5}$I$_5$] presents a slow but progressive weight loss probably associated with the emission of HI adsorbed on the crystals. The decomposition of this compound starts at 276 °C. Only the hydrated (pnH$_2$)$_2$[Pb$_{1.5}$Br$_7$]·H$_2$O compound shows a weight loss of 1.8% corresponding to the loss of one uncoordinated water molecule in the temperature range 70−120 °C. In the same range of temperature, in the calorimetric measurements an endothermic event takes place, associated with an amount of energy ($\Delta H = 47.6$ kJ/mol) corresponding to the theoretical value found for the dehydration heat of one water molecule in hydrated crystals ($\Delta H = 54-59$ kJ/mol).[11,12]

Electrical Results. Figure 7 shows the electrical conductivity, σ, of the 2-methylpentane-1,5-diammonium compounds, at 1 and 60 min after the voltage application, as a function of the reciprocal absolute temperature. Figure 8 shows the same for (pnH$_2$)[PbCl$_4$].

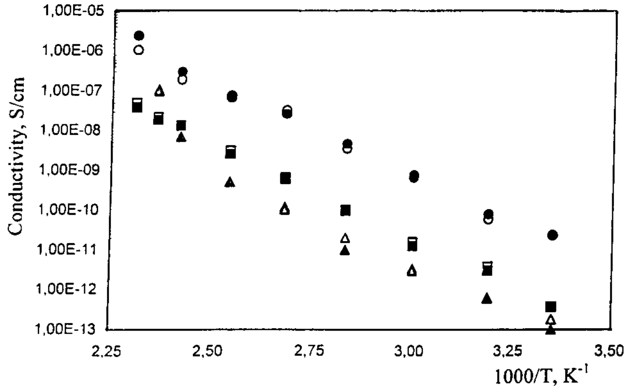

Figure 7. Electrical conductivity, σ, as a function of reciprocal absolute temperature, at 1 (open symbols) and 60 (solid symbols) min after voltage application for (2meptH$_2$)[PbCl$_4$] (triangles), (2meptH$_2$)[PbBr$_4$] (squares), and (2meptH$_2$)[Pb$_{1.5}$I$_5$] (circles).

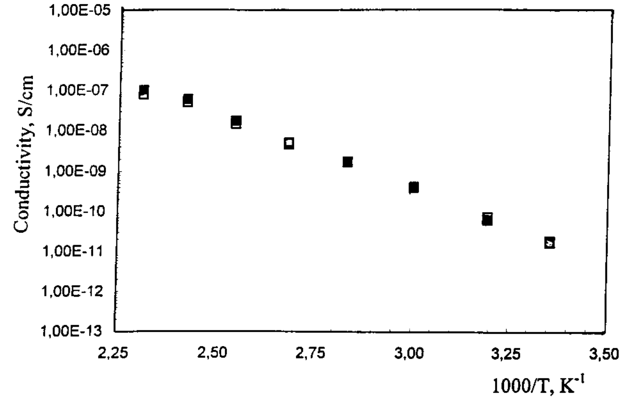

Figure 8. Electrical conductivity, σ, as a function of reciprocal absolute temperature, at 1 (open symbols) and 60 (solid symbols) min after voltage application for (pnH$_2$)[PbCl$_4$].

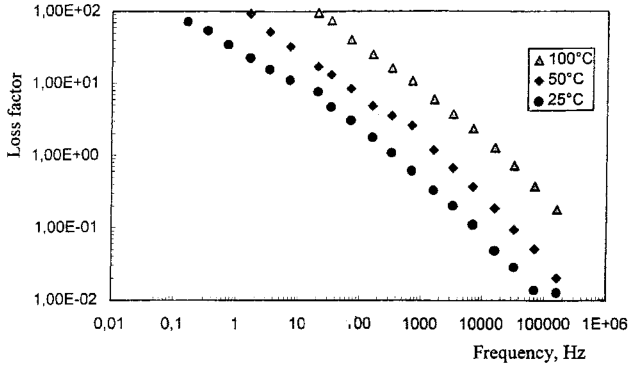

Figure 9. Loss factor, ϵ'', as a function of frequency for the (2meptH$_2$)[PbCl$_4$] compound.

The electrical behavior of (pnH$_2$)$_2$[Pb$_{1.5}$Br$_7$]·H$_2$O has not been investigated since the loss of the water moieties with increasing temperature causes unknown structural changes. The plots are almost linear for all compounds, except for the (2meptH$_2$)[PbCl$_4$] compound at highest temperatures, with an almost equal apparent activation energy; transient phenomena, as a function of time, are negligible. Figure 9 depicts loss factor values of (2meptH$_2$)[PbCl$_4$], as a function of frequency at different temperatures; the bromide and iodide compound plots have been omitted for brevity's sake, closely resembling the chloride plot. For the same reasons, the propane-1,3-diammonium plots have been omitted too. A strong dependence on frequency and temperature is found; such a steep increase with decreasing frequency is typical of ion-containing materials. An analogous dependence on frequency and temperature is found also for dielectric constants, not reported here for brevity's sake. As for other halometalates previously studied, conductivity seems again to be mainly ionic: the main source of charge carriers is likely the protons involved in hydrogen bonding between halogen and nitrogen atoms. As for the piperidinium haloplumbates already studied,[4] the iodine compound is more conductive, 1 order of magnitude greater than the chloride and bromide ones, which exhibited comparable conductivity. The higher conductivity of the iodine compounds has been explained on account of the higher degree of freedom of the proton involved in hydrogen bonds with iodine. This is peculiar to the ionic type of conduction, especially considering that for similar complexes showing electronic conductivity,[13] iodine compounds have proved to have the lowest conductivities. The explanation still holds for propane-1,3-diammonium compounds: however, another structural aspect, the evolution from 1D to a 2D structure, must also be taken into account. Referring, instead, to the homologous chlorocadmates,[14,15] haloplumbates show similar dc and ac behavior, with an almost equal activation energy for conduction, but lower values of conductivity. This is consistent with literature data.

Conclusions. The structures of the compounds studied are unusual for lead(II) ions. Lead(II) can be considered an ideal candidate for investigating the changing behavior from the low-dimensional inorganic lattice to the three-dimensional molecular network. The possibility of obtaining different model type structures, such as one-dimensional linear chain, ribbonlike, and perovskite-like, is closely related to the availability of the halide atoms in bridging lead atoms. This disposability may be reduced when counterions, having different hydrogen-bonding capabilities and water molecules, are present in the lattice. The electrical behavior of the compounds considered closely resembles that of previously investigated chlorocadmates,[16,17] where the main charge carriers are protons involved in hydrogen bonds. Although an electronic contribution to charge transfer cannot be ruled out, an ionic mechanism of charge transfer can again be inferred in these compounds.

Supporting Information Available: Listings of anisotropic thermal parameters for (2meptH$_2$)[PbCl$_4$] (**1**) (Table S1), (2meptH$_2$)[PbBr$_4$] (**2**) (Table S2), (2meptH$_2$)[Pb$_{1.5}$I$_5$] (**3**) (Table S3), (pnH$_2$)[PbCl$_4$] (**4**) (Table S4), (pnH$_2$)$_2$[Pb$_{1.5}$Br$_7$]·H$_2$O (**5**) (Table S5), fractional atomic coordinates and equivalent isotropic thermal parameters for all the cited compounds (Tables S6−S10), and data collection and refinement parameters (Table S11). This material is available free of charge via the Internet at http://pubs.acs.org.

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