Raman Spectra of Polynuclear Hydroxo-compounds of Lead(II) Chloride

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Raman spectra are reported for a series of basic chlorides of lead(II) which have been shown in other studies to be important in some hydrothermal ore solutions and in lead corrosion in aqueous chloride media. Synthetic lead chloride hydroxide and the mineral laurionite are shown to have identical polymeric structures. The relation between this infinite folded-band structure and the cluster formulations of related perchlorate compounds is rationalized in terms of equilibria including small rings and linear chains. The similarity of the Raman spectrum of $(PbOH^+)_n(Cl^-)_n$ to those of $Pb_6Cl_4(OH)_8$ and $Pb_8Cl_4(OH)_{12}$ (or $PbCl_2{\cdot}3Pb[OH]_2$) indicate closely related structures in all three cases. Vibrational spectra are reported for $Cs_4[PbCl_6]$.

ULTRAVIOLET spectra of synthetic solutions of composition identical to the Atlantis II Deep 56 °C brine demonstrated [1] that basic lead chloride complexes are likely to be important in hydrothermal ore solutions and in geochemical transportation of lead. Also a recent study by Raman spectroscopy of lead corrosion in aqueous chloride media reveals [2] that passivating films of basic lead chlorides form on potentiostatted lead electrodes.

The nature of soluble polynuclear lead(II) perchlorate complexes has been extensively studied by potentiometric,[3] equilibrium-ultracentrifugation,[4] light-scattering,[5] solution and crystal *X*-ray scattering,[6-8] and vibrational-spectroscopic techniques.[9,10] The dominant species in aqueous solution are $[Pb_4(OH)_4]^{4+}$ and $[Pb_6(OH)_8]^{4+}$. The $[Pb_4(OH)_4]^{4+}$ ion has been shown [6,7] to exist as a tetrahedron of Pb atoms while $[Pb_6(OH)_8]^{4+}$ consists of lead atoms arranged at the corners of three face-sharing tetrahedra.[8]

In the present study, Raman and i.r. spectra are reported for lead chloride hydroxide (in both mineral and synthetic forms), Charreton's ' tribasic salt ' ($PbCl_2{\cdot}3Pb[OH]_2$),[11] and $Pb_6Cl_4(OH)_8$ which was precipitated from a solution containing the cluster cation $[Pb_6(OH)_8]^{4+}$. The only structural information available for these or related compounds is derived from the refined structure of lead hydroxide iodide.[12] In addition, vibrational-spectroscopic data are reported for $Cs_4[PbCl_6]$.

RESULTS AND DISCUSSION

Basic Lead Halides.—Raman spectra of $(PbOH)_nCl_n$, $(PbOH)_nBr_n$, $Pb_6Cl_4(OH)_8$, and $Pb_8Cl_4(OH)_{12}$ (or $PbCl_2{\cdot}3Pb[OH]_2$) are given in Table 1. The absence of absorptions assignable to lattice water [13] at *ca.* 1 600 cm^{-1} in the i.r. spectra of these compounds indicated that they should be formulated as hydroxo- rather than hydrated oxo-compounds. The latter type of group has been identified [8] in the crystal structure of $Pb_6O(OH)_6(ClO_4)_4{\cdot}H_2O$.

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We prefer to interpret intense low-frequency lines in the spectra of the basic chlorides as arising from lattice and bending vibrations rather than lead–lead interactions as invoked by Maroni and Spiro [9,10] to explain aspects of the spectra of $[Pb_4(OH)_4]^{4+}$ and $[Pb_6(OH)_8]^{4+}$ in the solid state and in solution. *X*-Ray analyses of the structures of these cations [8] indicate that Pb–Pb distances are *ca.* 0.385 or 0.036 nm longer than the internuclear distance in metallic lead.[14]

Lead halide hydroxides. The structure of lead hydroxide iodide, which is closely related to the structure of lead chloride hydroxide, consists of infinite folded bands of $(PbOH^+)_n$ linked by iodide ions.[12,15] A comparison (Table 1) of the Raman spectrum of $(PbOH)_nCl_n$ with that of $(PbOH)_nBr_n$ indicated that at least two bands (at 331 and 276 cm^{-1})are insensitive to a change in the anion and consequently are assigned to vibrations of the $(PbOH^+)_n$ folded band. Further, two lines at lower frequency (90 and 50 cm^{-1}) appear to have counterparts in the spectra of the ions $[Pb_4(OH)_4]^{4+}$ and $[Pb_6(OH)_8]^{4+}$ (Table 1) and so are tentatively ascribed to vibrations of the polymeric cation. Infrared spectra of $(PbOH)_nCl_n$ and $(PbOH)_nBr_n$ also reveal three intense i.r. absorptions (Table 2) in the 200—700 cm^{-1} region which are insensitive to change of halide anion. One of these absorptions (at 588 cm^{-1} for the chloride) has been attributed [16] to OH bending because of its displacement in the spectrum of $(PbOD)_nCl_n$ (Table 2). The i.r. absorption at 340 cm^{-1} and the Raman lines at 331 and 276 cm^{-1} are tentatively attributed to Pb–O stretching vibrations of the polymeric cation, $(PbOH^+)_n$, because the latter are the highest-frequency features of significant intensity in the metal–ligand region of the spectrum.

Assuming an identical space group ($Pnma, D_{2h}^{16}$) and unit cell [12] for $(PbOH)_nCl_n$ as for $(PbOH)_nI_n$, the site symmetry of the Pb_2O_2 repeat unit can be identified as being C_i. A repeat unit analysis [17,18] predicts $5A_g$ and $3A_u$ vibrations after deletion of the axial rotation of the polymer band (A_g). Mutual exclusion is predicted with the A_g modes being Raman active and the A_u i.r. active. The observation of four possible Raman lines and two i.r. absorptions attributable to the Pb_2O_2 repeat unit (see earlier) is in reasonable accord with this analysis. The absorption at 340 cm^{-1} and the Raman line at 331 cm^{-1} are assumed to be non-coincident.

TABLE 1

Raman spectra * (cm^{-1}) of polynuclear hydroxolead(II) compounds

Compound									
$[Pb_4(OH)_4]^{4+}$	505	455	404	340	136			84	60
$[Pb_6(OH)_8]^{4+}$		455	386	365	144			*ca.* 90	68
$(PbOH)_nCl_n$			331m,sp	276m,sp		125(sh)	110vs,sp	90m,sp	50s,sp
$(PbOH)_nBr_n$			330m,sp	266m,sp		99s,sp	78vs,sp [73(sh)]	83s,sp	
$Pb_6Cl_4(OH)_8$		435vw,br	322m,br	274m,br	140vs,sp				
$Pb_8Cl_4(OH)_{12}$		430vw,br	325m,sp	299m,sp	141vs,sp				

* s = Strong, m = medium, w = weak, sh = shoulder, br = broad, sp = sharp, and v = very. Vibrational spectra of $[Pb_4(OH)_4]^{4+}$ and $[Pb_6(OH)_8]^{4+}$ are from refs. 9 and 10.

TABLE 2

Vibrational bands (cm^{-1})[a] of the Pb_2O_2 repeat unit

	$(PbOH)_nCl_n$		$(PbOD)_nCl_n$	$(PbOH)_nBr_n$	
Species	Raman	I.r.	I.r.[b]	Raman	I.r.
A_u		340	330		335
A_g	331			330	
A_g	276			266	
A_u		237			227

[a] Additional lines at lower frequency may also be associated with the Pb_2O_2 unit. [b] See ref. 16. Spectra were reported for the 300—800 cm^{-1} region.

Addition of chloride to a solution containing predominantly the cluster cation $[Pb_4(OH)_4]^{4+}$ precipitated a solid with the empirical formula PbCl(OH) (see Experimental section). The Raman and i.r. spectra and *X*-ray powder patterns of this solid were identical with those for lead chloride hydroxide (prepared by conventional methods [19]) and for the mineral laurionite [20] which has the stoicheiometry PbCl(OH). The conversion of the tetrahedral cluster structure of $[Pb_4(OH)_4]^{4+}$ into the infinite folded band structure of $(PbOH^+)_n(Cl^-)_n$ may be a consequence of small ring (cluster)–linear chain (folded band) equilibria in the perchlorate solutions. The insolubility of the folded-band halide polymers may displace the equilibrium away from the cluster ions on halide addition. Such small ring–linear chain equilibria are a general feature of inorganic polymers.[21] Minimal structural reorganization is required for the cluster to folded-band conversion as both structures can be viewed [8,12] as being composed of edge-linked triangles of lead atoms with hydroxo-groups located away from the centre of each triangular face (see Figure 1).

The compounds $Pb_6Cl_4(OH)_8$ *and* $Pb_8Cl_4(OH)_{12}$. The most significant feature of the Raman spectra of $Pb_6Cl_4(OH)_8$ and $Pb_8Cl_4(OH)_{12}$ (or $PbCl_2 \cdot 3Pb[OH]_2$) is that they give rise to a pair of Raman lines in the 270—330 cm^{-1} region which closely resemble two vibrational frequencies associated with the Pb_2O_2 repeat

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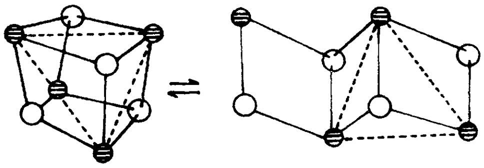
unit in the same region of the spectra of $(PbOH)_nX_n$. This observation favours the reformulation of $Pb_6Cl_4(OH)_8$ and $Pb_8Cl_4(OH)_{12}$ as folded-band structures. These structures probably differ from the latter compound in having a higher degree of hydroxo-group crosslinking between adjacent parallel folded bands. This crosslinking would account for the very low solubility of these compounds and for the appearance of additional lines [430 and 141 cm^{-1} for $Pb_8Cl_4(OH)_{12}$] which do not appear in the spectra of $(PbOH)_nX_n$.



Equilibrium between $[Pb_4(OH)_4]^{4+}$ (cluster) and $[Pb_n(OH)_n]^{n+}$ (folded bands). The latter structure is represented by a $Pb_4[OH]_4$ fragment of the infinite polymer. The triangular arrangement of Pb atoms common to both structures is shown in dotted outline

The above observations lead to the conclusion that these cluster and folded-band compounds constitute a family of basic salts (Table 3) with the general formula $2PbX_2{\cdot}2nPb[OH]_2$ (n = 1—3). The pH of the solutions from which the salts precipitate correlates, as expected, with the proportion of $Pb[OH]_2$ in the basic salt formulae.

TABLE 3

Lead hydroxo-complexes

Cluster	Folded band	Basic salt	n_{OH}/n_{Pb}	pH *
$[Pb_4(OH)_4]^{4+}$	$Pb_nCl_n(OH)_n$	$2PbCl_2{\cdot}2Pb[OH]_2$	1.00	3
$[Pb_6(OH)_8]^{4+}$	$Pb_{6n}Cl_{4n}(OH)_{8n}$	$2PbCl_2{\cdot}4Pb[OH]_2$	1.33	9
	$Pb_{8n}Cl_{4n}(OH)_{12n}$	$2PbCl_2{\cdot}6Pb[OH]_2$	1.50	10
		$Pb[OH]_2$	2.00	12

* Approximate pH at which precipitation occurs.

Caesium Hexachloroplumbate(II).—The Raman spectrum of $Cs_4[PbCl_6]$ (which is known [22] to contain $[PbCl_6]^{4-}$ units) includes intense lines at 204 and 119 cm^{-1} and a less-intense feature at 95 cm^{-1}. The far-i.r. spectrum exhibited a very broad intense absorption at *ca.* 130 cm^{-1} together with a sharper band at 63 cm^{-1}. The spectrum resembles, but is displaced to lower frequencies from, that [23] for $Rb_2[PbCl_6]$ and it may be assigned by analogy with the latter compound (Table 4). The stretching force constants calculated using the FG matrix method [24] were 127 N m^{-1} for the lead(IV) compound and 49 N m^{-1} for the lead(II) compound. The latter parameter is unusually low for a hexachlorometal compound.[25] Yeranos and Graham [26] correlated a decrease in stretching force constant for tetrahalides with a decrease in percent ionic character. This would lead to the conclusion that the lead(IV) compound is the more ionic, which is in apparent conflict with qualitative evidence, *viz.* the typically covalent properties of liquid $PbCl_4$ compared with the ionic lattice [27] of solid $PbCl_2$. The breadth of the far-i.r. absorptions for $Cs_4[PbCl_6]$ can probably be related to the ionic nature of the lattice. Clearly the relation between the force constant and ionic character, at least in this case, is not a simple one.

TABLE 4

Vibrational spectra (cm^{-1}) of $Rb_2[PbCl_6]$ and $Cs_4[PbCl_6]$

Assignment	$Rb_2[PbCl_6]$ [a]	$Cs_4[PbCl_6]$
$\nu_1(A_{1g})$	293	204
$\nu_2(E_g)$	220	119
$\nu_3(F_{1u})$	281	130
$\nu_4(F_{1u})$	139	63
$\nu_5(F_{2g})$	147	95
$\nu_6(F_{2u})$	83	[b]

[a] See ref. 23. [b] Inactive in i.r. and Raman.

EXPERIMENTAL

All syntheses described below were in a nitrogen atmosphere in order to prevent the formation [19] of lead carbonato-complexes from atmospheric CO_2. Because of the potential complexity of the solution equilibria,[3] complete precipitation of lead complexes was avoided and consequently no yields were recorded. The $PbCl_2$ used in this study was a Univar laboratory reagent. The $PbBr_2$ was prepared by the addition of a slightly acidified aqueous solution of KBr to a saturated solution of $Pb[NO_3]_2$. Both reagents were recrystallized and analyzed.

Precipitation from Cluster-cation Solutions.—Solid sodium chloride (1.0 g, 0.017 mol) was added to each of two solutions {prepared and characterized previously [1,9] containing predominantly $[Pb_4(OH)_4]^{4+}$ (5 cm^3) and $[Pb_6(OH)_8]^{4+}$ (5 cm^3)}. The white precipitate from the $[Pb_4(OH)_4]^{4+}$ solution was washed with dilute hydrochloric acid (pH 3) while the yellow precipitate, $Pb_6Cl_4(OH)_8$, was washed with dilute sodium hydroxide (pH 10). Analyses were obtained [28] for lead as lead chromate and for chloride by Volhard titration (Found: Cl, 13.5; Pb, 79.5. Calc. for ClHOPb: Cl, 13.7; Pb, 79.8. Found: Cl, 8.9; Pb, 82.1. Calc. for $H_8Cl_4O_8Pb_6$: Cl, 9.3; Pb, 81.7%).

Preparation of $PbCl_2{\cdot}3Pb[OH]_2$.—Following the method of Charreton,[11] sodium hydroxide (*ca.* 0.1 mol dm^{-3}) was added to a $PbCl_2$ solution (2.0 g of $PbCl_2$ in 200 cm^3, 7.2 mmol) containing added NaCl (0.5 g, 9 mmol) until the pH stabilized at *ca.* 10.5. The yellow precipitate was filtered and washed with dilute sodium hydroxide (pH 10.5) (Found: Cl, 7.2; Pb, 83.3. Calc. for $H_6Cl_2O_6Pb_4$: Cl, 7.1; Pb, 82.7%).

Preparation of Lead Halide Hydroxides.—Following the method of Yadava *et al.*[19] sodium hydroxide (40 cm^3, 0.1 mol dm^{-3}) was added to PbX_2 (X = Cl or Br) solution (1 dm^3, 0.01 mol dm^{-3}). The precipitate was washed with dilute HX solution (pH 3) (Found: Cl, 13.6; Pb, 80.1. Calc. for HClOPb: Cl, 13.7; Pb, 79.8. Found: Br, 25.6; Pb, 68.1. Calc. for HBrOPb: Br, 26.0; Pb, 68.1%).

Caesium hexachloroplumbate(II) was prepared, identified, and analyzed in a previous study.[1]

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Laser Raman spectra of the five solid compounds described above and a sample of the mineral laurionite were recorded using a Cary 81 spectrometer coupled to Coherent Radiation Laboratories 52G argon-ion and 500K krypton-ion lasers. Exciting lines employed in the study were 514.5 (Ar^+) and 647.1 nm (Kr^+). Spectra of solids were recorded using 90° unfocused laser illumination. Infrared spectra in the 200—4 000 cm^{-1} region were obtained for mulled samples using Jasco IRA-1 and IR-F spectrometers. Spectra were calibrated using conventional standards: indene (Raman), polystyrene (i.r., 700—4 000 cm^{-1}), and water vapour (i.r., 200—700 cm^{-1}). The far-i.r. spectrum of $Cs_4[PbCl_6]$ was recorded using a Hitachi–Perkin-Elmer FIS-3 spectrometer (Australian National University). *X*-Ray powder patterns were obtained on a Geigerflex diffractometer.

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