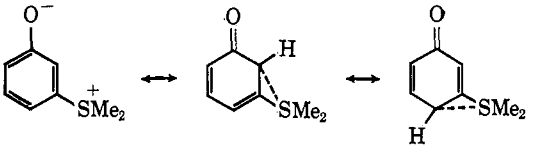
Table II. Calculation of α in Ground and Excited States

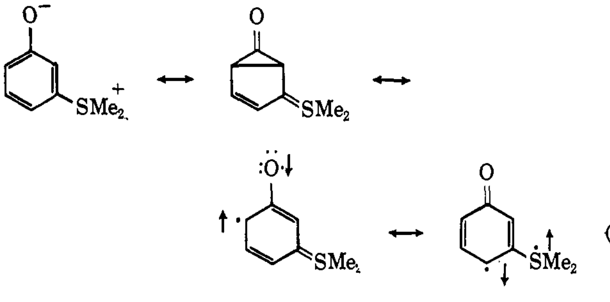
Substituent	σ_I	α	α^S	α^T
SO_2CH_3	0.59	0.18	0.8	0.5
$SOCH_3$	0.52	0.16	0.7	0.6
SCH_3	0.25	0.31	0.3	0.2

further evidence that no net enhancement of conjugation is noted in photoexcited aryl sulfides unless p_π-donor resonance is sterically unfavorable. It would be most interesting to compute α values for hindered sulfides; unfortunately, however, attempts to prepare hindered derivatives of *m*-hydroxythioanisole were not successful.



(4)

Direct conjugation between the phenolic group and sulfonium function may be responsible to some unusual frequency shifts in the ultraviolet spectra of *m*-dimethylsulfoniophenol. It has previously been assumed[31] that conjugative interactions in that compound involve canonical forms with external three-membered rings, particularly in photoexcited states. The present results suggest that conjugation in *m*-sulfoniophenols is not significantly different from that exhibited in excited singlet states of other *meta*-substituted phenols, in which "Dewar structures" are considered to make important contributions. This similarity suggests that the postulation of canonical forms with external three-membered rings in excited states of *meta*-substituted sulfonium salts is unnecessary. A more suitable description of the first excited singlet of these compounds would involve contributions from (*inter alia*) structures such as those in eq 5. The essential point is that, while any description of excited-state charge distributions in terms of contributing structures is likely to be highly imprecise, descriptions based solely upon data obtained from absorption spectra should be viewed with particular reservation.[20]



(5)

Acknowledgments. This research was supported in part by Grant 547-G2 from the Petroleum Research Fund, administered by the American Chemical Society. Thanks are extended to M. E. Roselli for assistance in obtaining some preliminary spectral data and to D. R. Johnson and J. N. Grote for assistance in synthesis of compounds.

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(31) See Table I, footnote *k*.

Vibrational Spectra of Polynuclear Hydroxy Complexes of Lead(II)[1a]

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Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey. Received May 28, 1966

Abstract: Raman spectra for solutions and Raman and infrared spectra for crystals containing polynuclear hydroxy complexes of lead(II) are reported. The close similarity of Raman spectra for solutions and crystals indicates the presence of identical structural units in the two phases, for a hydroxyl:lead ratio of both 1.00 and 1.33. In the former case, where $Pb_4(OH)_4^{4+}$ is the complex present, the vibrational features are entirely consistent with the tetrahedral structure previously proposed on the basis of solution X-ray scattering measurements. In the latter case, where the complex is probably $Pb_6(OH)_8^{4+}$, the spectrum is interpretable on the basis of an octahedral structure, although other structures are not excluded. There is no vibrational evidence of perchlorate binding to any of the lead species, either in solution or in the crystals.

Recently we presented the results of an infrared and Raman spectroscopic investigation of a polynuclear product of bismuth(III) hydrolysis.[2] We now wish to report on a similar study of the hydrolytic polymers of lead(II).

Lead(II) is isoelectronic with bismuth(III), and they share the convenient characteristic that their hydrolysis leads predominantly to the formation of a single polynuclear complex which is highly soluble in water. Whereas, however, for bismuth(III) the main product is

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(1) (a) This investigation was supported by the Public Health Service under Grant GM-13498-01 from the National Institute of General Medical Sciences. (b) NASA Predoctoral Fellow.

(2) V. A. Maroni and T. G. Spiro, *J. Am. Chem. Soc.*, **88**, 1410 (1966).

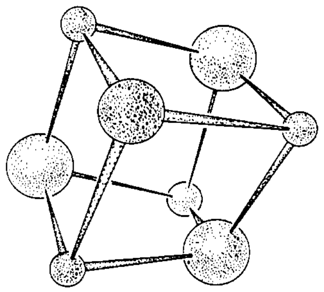

Figure 1. Structure proposed by Esval for $Pb_4(OH)_4^{4+}$, redrawn from ref 8. Lead and oxygen atoms are represented by the small and large circles, respectively.

$Bi_6(OH)_{12}^{6+}$, for lead(II) it is $Pb_4(OH)_4^{4+}$. This is the conclusion of several potentiometric studies[3–5] and has been strongly supported by equilibrium ultracentrifugation[6] and light scattering[7] measurements. Furthermore, Esval[8] has carried out an X-ray scattering investigation of a solution containing predominantly this tetramer. The resulting radial distribution function is interpreted in terms of three Pb–Pb interactions at 3.83 A and six Pb–O interactions at 2.57 A. Figure 1 shows the structure proposed on this basis: a distorted cube consisting of lead and oxygen atoms arranged tetrahedrally. A similar structure has been determined[9] for the closely related thallium(I) methoxide.

Although $Pb_4(OH)_4^{4+}$ is the main product, $PbOH^+$ and possibly Pb_2OH^{3+} are formed at low degrees of hydrolysis.[3] In addition, clear solutions can be prepared with a hydroxyl:lead ratio of 1.33. Olin's careful potentiometric measurements are interpretable in this region in terms of an equilibrium[3] between $Pb_3(OH)_4^{2+}$ and $Pb_6(OH)_8^{4+}$. Esval and Johnson's ultracentrifugation data[6] also show degrees of polymerization tending toward six at higher concentrations in this region.

Experimental Section

Hydrolyzed lead(II) solutions were prepared by dissolving appropriate quantities of reagent grade lead oxide (Matheson Coleman and Bell) in concentrated perchloric acid with sufficient digestion to complete dissolution. They were analyzed for lead by precipitation as the sulfate and for perchlorate by passage through a cation-exchange resin in the acid form and titration of the liberated acid. Solution I was 4.47 *M* in lead and 4.63 *M* in perchlorate, corresponding to a hydroxyl:lead ratio of 0.960. This solution was similar to the one used by Esval for his X-ray measurements.[8] In it essentially all of the lead should be present as $Pb_4(OH)_4^{4+}$. Solution II was 5.72 *M* in lead and 7.50 *M* in perchlorate (OH:Pb = 0.688). Solution III was 4.82 *M* in lead and 9.64 *M* in perchlorate; in this solution the lead should be essentially unhydrolyzed. The solutions, which were kept free of carbon dioxide to prevent carbonate precipitation, were filtered through a fine-glass frit under nitrogen pressure and transferred to a standard Cary 7-mm Raman liquid cell, and their spectra were recorded at 28 ± 1° on a Cary Model 81 Raman spectrophotometer using the 4358-A mercury line for excitation. Solutions I and II were slightly supersaturated, and some crystals formed on long standing. Their spectra, however, were the same (except for absolute intensity) after several weeks as when the solutions were freshly prepared.

Crystals were obtained from solution I by slow evaporation and dried over sodium. Their Raman spectrum was taken in a conical cell on the design of Busey and Keller.[10] Their infrared spectrum was obtained in a Nujol mull pressed between polyethylene windows. The region 650–180 cm^{-1} was scanned with a Beckman IR-12 infrared spectrophotometer, and measurements in the region below 180 cm^{-1} were made with an RIIC FS-520 interferometer.

In addition crystals containing 1.33 hydroxyls/lead were obtained, following the procedure of Willard and Kassner,[11] from a solution prepared by filtering excess lead oxide from a mixture which had been made up from 2 moles of lead oxide/mole of concentrated perchloric acid and which had been refluxed for 1 day. They were dried over sodium and their Raman and infrared spectra were obtained as above. These crystals are significantly soluble only in hot water, and a crude Raman spectrum was obtained from a hot solution before recrystallization began.

Results

The Raman spectrum of solution I (Figure 2a) shows, in addition to bands due to perchlorate, strong scattering at 404, 130, and 87 cm^{-1}, the first two bands being strongly polarized. There are weak emissions at *ca.* 60 and 350 cm^{-1}. In addition the 462-cm^{-1} perchlorate band is significantly enhanced, the integrated intensity ratio of this band to the perchlorate band at 620 cm^{-1} (independent of the polarization of the incident radiation) being 1.17, as compared to the value of 1.09 found for sodium perchlorate and barium perchlorate solutions. The Raman spectrum of the crystals obtained from solution I is shown in Figure 2b and is seen to be substantially the same as the solution spectra. All of the solution bands occur at essentially the same frequency in the solid spectrum which, in addition, shows a sharp band at 455 cm^{-1} on the low-frequency side of the perchlorate band. Presumably this emission is not resolved from the perchlorate band in solution but simply contributes to its enhanced intensity. (Weak emissions at 145 and 170 cm^{-1} occur in all solid spectra and are considered part of the background.) The infrared spectrum of the solid in the 650–180-cm^{-1} region (Figure 3a) contains, in addition to the 620-cm^{-1} perchlorate band, a prominent absorption centered at 349 cm^{-1} and a somewhat weaker absorption at 505 cm^{-1}. Below 180 cm^{-1} the infrared spectrum contains only a broad absorption in the 100–40-cm^{-1} region.

The Raman spectrum of the crystalline material containing 1.33 hydroxyls/lead is shown in Figure 2c. Although closely related to the spectrum of the crystals obtained from solution I, it shows significant differences. The 455-cm^{-1} band remains at the same frequency but is considerably enhanced; the 404-cm^{-1} band shifts down to 386 cm^{-1}; and the 136, 84, and 60 cm^{-1} bands all shift up, to 144, 90, and 68 cm^{-1}, respectively. Furthermore, the infrared band found at 349 cm^{-1} in the crystals from solution I is now centered at 365 cm^{-1} and shows evidence of splitting into three components (Figure 3b). The band at *ca.* 505 cm^{-1} is absent. The Raman spectrum of the hot solution containing 1.33 hydroxyls/lead was of poor quality, but the strong crystal bands at 386 and 144 cm^{-1} showed up at the same frequencies, and the

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(3) A. Olin, *Acta Chem. Scand.*, **14**, 126, 814, 1999 (1960); *Svensk Kem. Tidskr.*, 73, 482 (1961).

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(10) R. H. Busey and O. L. Keller, *J. Chem. Phys.*, **41**, 215 (1964).

(11) H. H. Willard and J. L. Kassner, *J. Am. Chem. Soc.*, **52**, 2391 (1930).

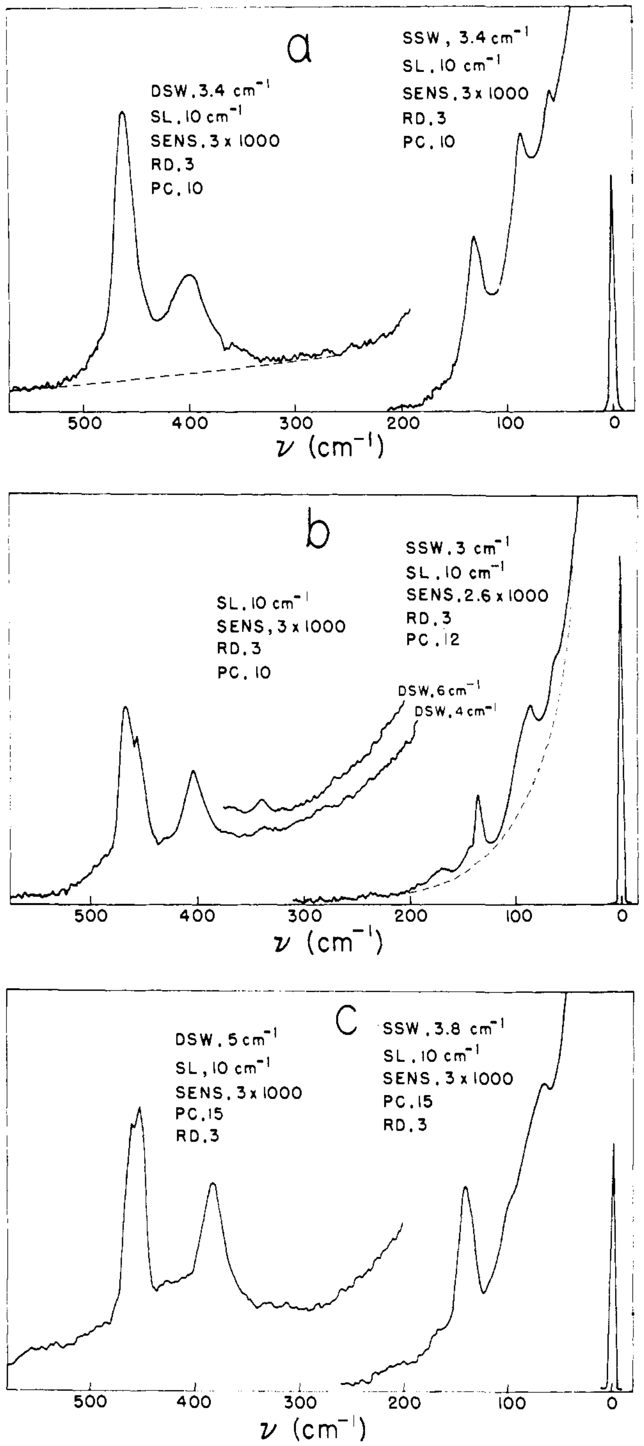

Figure 2. Raman spectra of (a) solution I, (b) crystals containing 1.00 hydroxyl/lead, (c) crystals containing 1.33 hydroxyls/lead; Cary Model 81: lamp current 15 amp; scan speed 0.25 cm^{-1}/sec. Abbreviations: SSW, single slit width; DSW, double slit width; SL, slit length; PC, period control; SENS, sensitivity setting; RD, Raman dynode setting.

weaker band at 90 cm^{-1} appeared as a shoulder on the exciting line.

The Raman spectrum of solution II showed the same bands as for solution I and at the same relative intensity. That of solution III showed bands due to perchlorate ion but no other feature except for a single broad weak band at *ca.* 290 cm^{-1}. The integrated intensity ratio of the perchlorate band at 462 cm^{-1} relative to that at 620 cm^{-1} is 1.06, as compared to 1.09 for sodium perchlorate solutions.

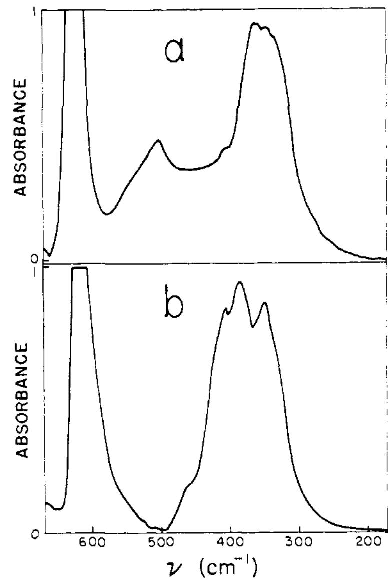

Figure 3. Infrared spectra of (a) crystals containing 1.00 hydroxyl/lead, (b) crystals containing 1.33 hydroxyls/lead, in Nujol mull; Beckman IR-12; double beam; gain, 6%; slit program, standard; period control, 8.

Discussion

The Raman spectra all show perchlorate bands occurring at the frequencies expected for the free ion.[12] In addition, the infrared spectra of the solids contained the 620-cm^{-1} ν_4 perchlorate band but not the ν_2 band (infrared inactive for free perchlorate, active when bound) at 462 cm^{-1}. Consequently there is no vibrational evidence for perchlorate binding to the lead species either in the solutions or in the solids.

Since there is no change in the relative intensities of the solution Raman bands attributable to lead species on going from a hydroxyl:lead ratio of 1.0 to 0.7, it appears that they all arise, as expected, from a single complex. From the close similarity between the Raman spectra of solution I and of the crystals obtained from solution I we can infer that they both derive from the same structural unit which, on the basis of Esval's X-ray results,[8] can be assumed to be tetrahedral $Pb_4(OH)_4^{4+}$. For this species (point group T_d) the representation of the vibrational modes (neglecting hydrogen atoms) is $\Gamma_{vib} = 2A_1 + 2E + 3F_2$. All of these represent Raman-active vibrations, and the F_2 vibrations are also active in the infrared. The observed frequencies attributable to the tetramer are listed in Table I. We were able to find six of the seven predicted Raman bands and at least one of the three predicted infrared bands. The 349-cm^{-1} infrared band which shows weakly in the Raman is clearly one of the expected F_2 vibrations. We assign the weak band at *ca.* 60 cm^{-1} in the Raman to the same symmetry; this mode probably accounts for most of the infrared absorption between 100 and 40 cm^{-1}. The third expected F_2 vibration may be the band observed in the infrared at *ca.* 505 cm^{-1}; this

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(12) R. E. Hester and R. A. Plane, *Inorg. Chem.*, 3, 769 (1964).

band is not resolved in the Raman spectrum but is expected to be of low intensity and could be buried in the foot of the 462-cm^{-1} perchlorate band. Of the remaining Raman bands the two at 404 and 130 cm^{-1} are strongly polarized and clearly belong to the A_1 representations. The remaining two sharp bands at 455 and 87 cm^{-1} are then left for the two E vibrations.

Table I. Vibrational Frequencies (cm^{-1}) Attributable to $Pb_4(OH)_4^{4+}$[a]

Assignment	Raman Solution	Raman Solid	Infrared Solid
A_1	404 p	404	. . .
	130 p	136	. . .
E	NR, dp	455	. . .
	87 dp	84	NR
F_2	NR	NR	505 ?
	Ca. 350 dp	*Ca.* 340	349
	Ca. 60 dp	*Ca.* 60	NR

[a] Symbols: p. polarized; dp, depolarized; . . ., not observed; NR, not resolved.

The six observed frequencies are divided into two well-separated regions: 60–140 cm^{-1} and 350–500 cm^{-1}. As was suggested[2] in the case of $Bi_6(OH)_{12}^{6+}$, it seems likely that the higher frequency bands involve primarily Pb–O bond stretching, and that the low-frequency bands involve primarily angle bending. The totally symmetric bands at 404 and 130 cm^{-1} no doubt arise from the in-phase and out-of-phase breathing modes of the cubic cage.

The species present at 1.33 hydroxyls/lead are not so well defined as is the tetramer. Olin's results,[8] as corroborated by Esval and Johnson's ultracentrifuge data,[6] indicate that the predominant species at higher concentration should be $Pb_6(OH)_8^{4+}$. Although the solution Raman spectrum in this region is of poor quality, the observed coincidence of the two main bands in the solution and solid spectra does show that the same species is present in both phases. That the Raman spectrum in this region is related to that of the tetramer is not unexpected since the same atoms are involved and the force constants are not expected to change dramatically with changing hydroxyl number. However, the significant shifts in frequency and in relative intensity that do occur are indicative of a change in structure. At present there is no experimental evidence for distinguishing among the many possible structures for a species of composition $Pb_6(OH)_8^{4+}$. The simplest and most symmetrical structure would be one in which the six leads are at the corners of a regular octahedron and the eight hydroxyls are at the centers of the octahedral faces. This structure is well characterized in the case of $Mo_6Cl_8^{6+}$.[13] In such an octahedral cage the number of leads attached to each oxygen would still be three as in the tetramer, but the number of oxygens attached to each lead would be increased from three to four. For this structure (point group O_h) the representation of the vibrations active in the Raman or infrared would be (neglecting hydrogen atoms): $\Gamma_{vib} = 2A_{1g} + 2E_g + 3F_{2g} + 3F_{1u}$. Vibrations that are Raman active are represented by $2A_{1g} + 2E_g + 3F_{2g}$, and those active in the infrared are represented by $3F_{1u}$. From the point of view of the symmetry of the vibrational modes the situation is thus very similar to that of the tetramer, the major difference being that triply degenerate modes are no longer coincident in the Raman and infrared due to the center of symmetry in the octahedral model. Five of the seven expected Raman bands and one of the three expected infrared bands are observed in the crystal spectrum (Table II). The apparent splitting of the 365-cm^{-1} infrared band into three components suggests that it does indeed arise from a triply degenerate vibrational mode, the degeneracy being slightly lifted by crystal forces. The mutual exclusion rule appears to hold, but this cannot be rigorously evaluated since the infrared band occurs at a frequency corresponding to the tail of the 386-cm^{-1} Raman band. We conclude that the vibrational spectrum is consistent with an octahedral structure but that it cannot be taken to exclude other less symmetrical structures.

Table II. Vibrational Frequencies (cm^{-1}) Attributable to Species Containing 1.33 Hydroxyls/Lead[a]

Raman Solution	Raman Solid	Infrared Solid
NR	455	. . .
388	386	. . .
. . .	. . .	365
144 p	144	
Ca. 90	*Ca.* 90	
NR	68	

[a] Symbols: p, polarized; . . ., not observed; NR, not resolved.

The broad weak Raman band observed for solution III at 290 cm^{-1} is probably a mode arising from aquolead(II). It is interesting that this frequency is considerably lower than those asssigned to other polyvalent aquometal ions,[14] most of which occur between 350 and 450 cm^{-1}. Although the 462-cm^{-1} perchlorate band obscures part of this region, its integrated intensity in solution III shows no enhancement relative to sodium perchlorate.

[13] C. Brosset, *Arkiv Kemi*, **1**, 353 (1949); *Arkiv Kemi, Min., Geol.*, **A20**, No. 7 (1945).

[14] R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 768 (1964).