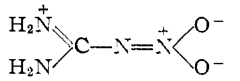
bending vibrations. The double bond stretching vibrations would be expected to give rise to the most intense bands. The bands resulting from N–H bending may be obscured in some cases by the double bond stretching bands since there is a common region around 6 μ where these bands may overlap.

The C=N stretching bands usually occur at shorter wave lengths than the nitro bands.[10] The probable assignments of the various bands in the 3 and 6 μ regions are given in Table I. If these compounds are nitrimines as recent work indicates,[1–5] then the C=N bond is conjugated with the nitro group and any contribution from forms with a separation of charge such as



$$\begin{matrix}\overset{+}{H_2N}\\ H_2N\end{matrix}\!\!>C-N=\overset{+}{N}<\begin{matrix}O^-\\ O^-\end{matrix}$$

will reduce the amount of double bond character in the imine double bond and also the amount of double bond character in the nitro group. The frequency of the corresponding bands will be lowered by such changes. One would then expect the frequency of the band corresponding to the nitro group to change in the same way as the one corresponding to the imine C=N group, and that these changes would be related to the relative contribution of the resonating forms with a separation of charge. The compound expected to have the greatest contribution of these forms is 2-nitroiminoimidazolidine since it has forms of equal energy and has a carbon and hydrogen attached to the nitrogens that assume the plus charge, instead of two hydrogen atoms. The C=N and nitro group in this compound should have the most single bond and the least double bond character and therefore the lowest frequencies. Such is the case with values of 1618 and 1567 cm.$^{-1}$ for these two bands.

1-Nitro-2-nitriminoimidazolidine would have less contribution from these forms since it has essentially only one form with a separation of charge and the frequencies here are 1642 and 1626 cm.$^{-1}$.

Nitroguanidine has forms of equal energy, but the H_2N-groups accept less readily the plus charge than a C–NH– group. Apparently the latter is the more important factor for the frequencies in this compound are 1664 and 1637 cm.$^{-1}$, indicating more double bond character in the C=N and the nitro group than in the previous compound.

Nitroaminoguanidine would be expected to have a smaller contribution from the forms with a separation of charge than nitroguanidine because the forms are no longer equivalent. Such is the case for the C=N band has a frequency of 1672 cm.$^{-1}$, but the nitro band in this case is anomalous being at 1623 cm.$^{-1}$. This may result from the large amount of hydrogen bonding reducing the frequency of the nitro group.

Nitrosoguanidine would be expected to have the least contribution from the forms with a separation of charge and its C=N group has the highest frequency 1689 cm.$^{-1}$ as anticipated. The nitroso frequency of 1504 cm.$^{-1}$ is higher than the usual unconjugated nitroso range.[10] But since conjugation causes the nitro group to absorb at higher frequencies,[10] the same behavior is likely for the nitroso group. The higher absorption frequency for the nitroso group thus indicates that the nitrimine structure for this compound is correct. The behavior of the bands around 6 μ in all these compounds supports the other extensive evidence that the compounds are nitrimines.

I wish to express my appreciation to Professor Richard M. Badger for his expert advice and counsel during the entire course of this investigation, and to Professor George F. Wright for supplying five of the compounds.

SAN FRANCISCO 22, CALIFORNIA

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(10) Reference 7, pp. 140–141.

[CONTRIBUTION FROM THE UNIVERSITY OF ARKANSAS INSTITUTE OF SCIENCE AND TECHNOLOGY]

Lead Salts of 2,4,6-Trinitroresorcinol

BY RALPH A. ZINGARO

RECEIVED SEPTEMBER 23, 1953

A method for the preparation of pure normal and basic lead styphnate is described, and two new salts, including dipyridinlead(II) styphnate, have been prepared. A study of some of the physical properties of these salts and a consideration of the chemistry involved in their preparation raises a question as to the structure of these salts. Structures for these compounds, based on the observations reported, are discussed. The infrared spectra of normal and basic lead styphnate and of styphnic acid have been measured, and observations relating to them are reported.

Although lead salts of styphnic acid (2,4,6-trinitroresorcinol) have been known for many years and have found extensive military and commercial use as electrical initiators for explosive charges, little effort has been devoted to a better understanding of their chemical nature. The information relating to them is confined very largely to the patent literature and is concerned almost wholly with commercial preparation methods.

Griess[1] reported a basic salt of lead styphnate to which he assigned the formula $C_6H(NO_2)_3O_2Pb\cdot PbO\cdot 1^1/_2H_2O$, and Herz[2] claimed the first preparation of anhydrous, normal lead styphnate. There are a variety of patented procedures for the preparation of a normal salt hydrate and a basic salt for which structures I and II[3] have been generally accepted. The preparation of these salts, as usually described, involves the direct combination of solutions of a soluble lead salt and an alkali (or alkaline earth) metal styphnate. The conditions of *p*H,

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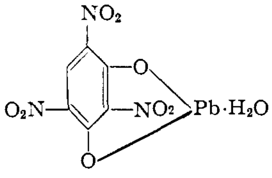
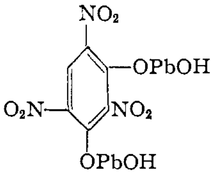
(1) P. Griess, *Ber.*, **7**, 1224 (1874).

(2) E. Herz, U. S. Patent 1,443,328 (1919).

(3) J. Taylor, "Detonation in Condensed Explosives," Oxford University Press, New York, N. Y., 1952, p. 13.



I



II

temperature, and rate and order of addition are highly critical and depend upon the specific directions being followed.

The present investigation was undertaken because of our need for a reproducible source of pure lead styphnate. Preparations carried out under directions available to us did not yield a satisfactory product. As a result, a new preparative method, which gave an easily-reproducible, highly-crystalline material, was developed. In order to obtain additional information about their structure and chemical nature, the infrared spectra, powder X-ray diffraction patterns, and dehydration of these salts were investigated. The studies have raised several questions concerning the structure of these compounds, and alternative structures are considered herein. During the course of the investigation several pyridine-bearing lead styphnate derivatives were prepared.

Experimental

Materials.—The styphnic acid, ethanolamine and pyridine were Eastman Kodak Co. white-label chemicals and were used without further purification. The lead nitrate was C.P. grade.

Normal Lead Styphnate.—To a solution containing 2.45 g. (0.01 mole) of styphnic acid in 50 ml. of ethanol was added 50 ml. of 0.20 *M* aqueous lead nitrate solution. This was heated to 70° and this temperature was maintained throughout the course of the reaction. Ethanolamine was then added dropwise with stirring, allowing the precipitate which formed after the addition of each drop, to redissolve. This addition was continued until the *p*H tested 3.5 to 4, indicated by Hydrion test paper. An additional 50 ml. of ethanol was then added and the solution was brought back to reaction temperature. This was followed by the dropwise addition of a 4.0 *M* solution of ethanolamine in ethanol. Upon the addition of each drop there was formed a flocculent, yellow precipitate which changed into orange, crystalline normal lead styphnate on stirring. The addition of the dilute ethanolamine should be carried out slowly over a period of one hour, and the addition should be made only after the yellow precipitate has been completely converted to the orange, crystalline product. The volume of the solution should be maintained at about 150 ml. at all times. The reaction should not be continued above *p*H 4.8 as higher *p*H values will cause contamination by basic impurities. The final product is thoroughly washed with water and ethanol and separates in the form of orange, hexagonal crystals.[4]

Anal. Calcd. for $C_6H(NO_2)_3O_2Pb\cdot H_2O$: Pb, 44.24; N, 8.97; C, 15.38. Found: Pb, 44.32; N, 8.93; C, 15.51.

Basic Lead Styphnate.—To a solution containing 7.0 g. (0.021 mole) of lead nitrate in 70 ml. of water, there was added slowly with stirring, over a period of two hours, a solution containing 2.45 g. (0.01 mole) of styphnic acid and 1.6 g. (0.04 mole) of sodium hydroxide in 80 ml. of water. The reaction temperature was maintained at 65 to 70° and the mixture was stirred for approximately one hour after the addition was complete. The bright yellow amorphous precipitate which formed immediately upon addition of the sodium styphnate was converted to yellow needles of basic lead styphnate which were filtered off and washed thoroughly with distilled water.

Anal. Calcd. for $C_6H(NO_2)_3(OPbOH)_2$: Pb, 59.94; N, 6.07; C, 10.42. Found: Pb, 60.01; N, 5.93; C, 10.48.

Dipyridinelead(II) Styphnate.—When anhydrous, normal lead styphnate was warmed in pure pyridine at 50° with stirring, the orange crystals were completely converted, after about an hour, into small, canary-yellow needles containing pyridine. The analysis corresponded to a molecule containing two moles of pyridine to each mole of lead styphnate.

Anal. Calcd. for $C_6H(NO_2)_3O_2Pb(C_5H_5N)_2$: Pb, 34.05; N, 11.51. Found: Pb, 34.21; N, 11.56.

The Reaction of Lead Nitrate with Styphnic Acid in the Presence of Pyridine.—To 100 ml. of a 0.10 *M* styphnic acid solution in ethanol, pyridine was added until the *p*H was 4.5. The solution was then diluted with an additional 100 ml. of ethanol and heated to dissolve the precipitate of pyridinium styphnate. To the clear, hot solution was added 100 ml. of 0.20 *M* aqueous lead nitrate. The solution remained clear for several days, after which time a slow deposition of yellow needles took place. These were filtered off and washed with water and alcohol and dried. Repetition of this experiment gave the same product, a pyridine-bearing lead styphnate analyzing as follows: Pb, 40.82; C, 20.20; N, 9.73. These crystals showed no loss of water even when heated *in vacuo* at 135° for 48 hours. This indicated that the compound probably was not a derivative of lead styphnate hydrate. A suggested formula which satisfies the analytical data and which does not require a water of hydration would be given by a basic salt of the type $C_6H(NO_2)_3OH(OPbOH)\cdot{}^1/_2C_5H_5N$. Attempts to produce analogous derivatives with either α- or β-picoline led only to the formation of unidentified products of varying composition.

Analytical.—All lead and nitrogen determinations were checked by outside analysts.[5] Nitrogen determinations were obtained using both the Dumas method and a modified Kjeldahl method, which involves the preliminary reduction of the nitro groups. The Dumas method gave much more satisfactory results. Because of the explosive nature of the materials, care must be used when the Dumas method is employed. The sample was spread over a large area of the temporary filling so that only a small amount was detonated at once.

Carbon determinations were run by the wet-way oxidation method[6] as direct combustion always caused violent decomposition of the sample.

The most satisfactory method for determining lead was by a simplified chromate method, developed in this Laboratory, which eliminates the preliminary digestion with mineral acids. A 0.1- to 0.2-g. sample is treated with 20 ml. of glacial acetic acid, 20 g. of ammonium acetate and 50 ml. of water, and the mixture is stirred with heating until the sample is completely dissolved. Another 100 ml. of water is then added and the solution is heated to just below the boiling point. A total of 8 ml. of saturated potassium bichromate solution is then slowly delivered by means of pipet at the rate of about 4 drops a minute with continual stirring. The lead chromate, after digestion for 30 minutes in the hot solution, should settle rapidly as a bright, red-orange precipitate, leaving a clear supernatant solution. The precipitate is collected in a fine sintered glass crucible, washed well with hot water, and dried at 120° for at least one hour. This procedure gave the best and most reliable results, but the method obviously is limited in the number of compounds to which it can be applied.

Infrared Spectra and X-Ray Diffraction.—The infrared pectra were run on a Perkin-Elmer model 21 spectrometer. All of the samples were ball-milled to a fine powder and were examined as Nujol mulls. They also were mulled in fluorolube and examined in this medium in order to observe spectral features obscured by the Nujol bands. No quantitative interpretation of the spectra was attempted. The powder X-ray diffraction patterns were obtained by means of a North American Philips High-Angle Goniometer.

Dehydration Studies.—Samples of approximately the same weight were suspended from one arm of an automatic

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(4) All the compounds described in this paper explode violently when subjected to heat, mechanical shock or static charge. Proper precautions should be exercised in handling them.

(5) Clark Microanalytical Laboratory, Urbana, Ill.; DuGood Laboratory, St. Louis, Mo.

(6) R. M. McCready and W. Z. Hassid, *Anal. Chem.*, **14**, 525 (1942).

recording balance,[7] and the loss in weight on heating was followed by means of a General Electric strip recorder.

Results and Discussion

The infrared spectra of both normal lead styphnate hydrate and of basic lead styphnate (curves A and B, Fig. 1) showed no absorption bands at frequencies above 1600 cm.$^{-1}$. In a recent investigation of the infrared spectra of a large number of inorganic solids, including more than 60 hydrates, Miller and Wilkins[8] reported that almost every hydrate possessed an absorption band in the 3100 to 3400 cm.$^{-1}$ region, and that the band probably resulted from the water of hydration. In the case of several hydrates, however (*e.g.*, monobasic calcium phosphate hydrate and copper selenite dihydrate), the existence of an absorption band in this region was not established. Although the absence of an absorption band for normal lead styphnate in this region presents a question as to the presence of water of hydration in this molecule, its absence in the molecule cannot be taken for granted. Water determinations by direct titration with the Karl Fischer reagent indicated only traces of moisture were present. These observations led us to reinvestigate the reversible dehydration of this compound reported by Stettbacher,[9] whose studies were made on compounds the analyses of which indicated they were of questionable purity. The results of our investigation as illustrated in Fig. 2 definitely confirm the findings of Stettbacher that normal lead styphnate does undergo a reversible loss of the elements of water. As expected, the rate of loss in weight becomes more rapid with increasing temperature. Attention is called to the 115° curve, where a break is indicated at the point corresponding to the loss of one-half mole of water. A hemihydrate has been reported[10]; however, neither of the other dehydration curves nor the rehydration curve shows any break at the point corresponding to the formation of the hemihydrate.

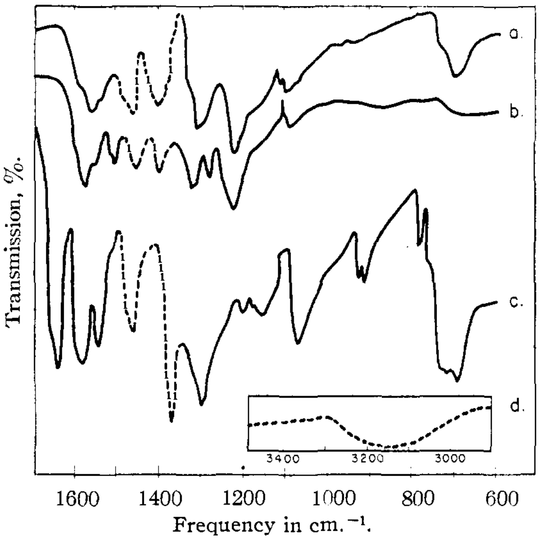

Fig. 1.—Infrared spectra of a, normal lead styphnate hydrate; b, basic lead styphnate; c, styphnic acid; d, styphnic acid, 2900–3500-cm.$^{-1}$ region. Nujol was used for the solid portion of the curves and fluorolube for the dotted portion.

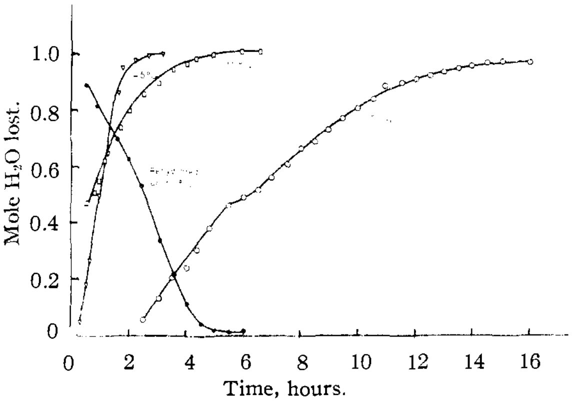

Fig. 2.—Rate of loss of water from normal lead styphnate hydrate at various temperatures. The curve represented by the solid circles levels off at a point corresponding to the regain of a mole of water by a dehydrated sample: ▽, 145°; □, 135°; ●, rehydrated at 30°; ○, 115°.

Analysis and examination of the infrared spectrum of a sample of normal lead styphnate after dehydration followed by rehydration showed that the final product was identical with the starting material. Lead analyses of six dehydrated samples gave values of 45.68 to 46.52% lead. The theoretical lead content of anhydrous normal lead styphnate is 46.10%. The dehydration studies and the analytical data, as well as the conversion of the dehydrated normal lead styphnate to dipyridinelead(II) styphnate, all indicate the existence of a true anhydrous, normal lead styphnate. It is questionable whether the anhydrous salt may be prepared directly from aqueous solution as claimed by Herz.[2]

The effects of heating on the crystalline structure of lead styphnate were observed by means of powder X-ray diffraction patterns and microscopic examination. The discrete, hexagonal crystals of normal lead styphnate turned red on heating, with the concurrent fracture of the crystals into irregular particles of greatly decreased dimensions. Upon rehydration, the red color of the anhydrous salt reverted back to the orange characteristic of the hydrate, but the appearance of the broken crystals remained unaltered. Although the initially prepared crystalline salt gave a powder X-ray pattern possessing many intense peaks arising from the crystal-orientation planes, after heating and rehydration the resulting sample yielded a pattern in which most of these peaks were completely lacking or very largely diminished. Although it was shown by means of infrared examination and analysis that this treatment does not change the molecular structure, it is apparent that the crystalline structure is severely affected. The observation of Miles[11] that

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(7) We are indebted to Dr. F. A. Mauer of the National Bureau of Standards for furnishing the circuit diagrams for the construction of the balance. See *Chem. Eng. News*, **31**, 2304 (1953).

(8) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

(9) A. Stettbacher, *Nitrocellulose*, **8**, 3 (1937).

(10) R. E. Kirk and D. F. Othmer, "Encyclopedia of Chemical Technology," Vol. 6, Interscience Publishers, Inc., New York, N. Y., 1951, p. 16.

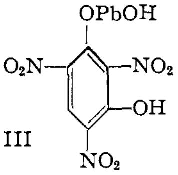
(11) F. D. Miles, *J. Chem. Soc.*, 2532 (1931).

dehydration brought about no change in the shape or clarity of crystalline normal lead styphnate was not verified.

If we consider the molecule of normal lead styphnate as represented by Structure I, the formation of covalent O–Pb–O bridge is implied. The formation of this bridge in the plane of the ring is immediately ruled out on steric grounds, because the presence of the large nitro group precludes the formation of covalent bonds, from the two oxygens ortho to it, to the common lead atom. The formation of an O–Pb–O bridge directed outside of the plane of the ring is highly improbable, as this would require a C–O–Pb bond angle of far less than 90° which is what is normally to be expected.[12]

It would appear more nearly correct to consider normal lead styphnate hydrate to possess an essentially ionic structure built of divalent lead ions and divalent styphnate ions. The water molecules must be strongly held within this network, both through coördination with the lead ions and by electrostatic forces within the ionic lattice. It is not unreasonable to assume, as suggested by Pauling,[13] that the styphnate ion will be stabilized by extra resonance energy relative to the un-ionized molecule, and this fact also would favor an ionic structure.

An alternative, based upon the tendency of lead to form basic salts, is given by structure III. Such a structure would explain satisfactorily the absence of a hydrate band in the infrared spectrum; the formation of the normal salt on heating could result from intermolecular loss of water.



III

There was no apparent loss of water by the basic salt even on extended heating at 135°. Because the preparation of the basic salt always is carried out above *p*H 5.5 and in solutions at least 0.2 *M* with respect to lead ion, the formation of lead hydroxide is to be expected. Hence, the structure as proposed by Griess[1] is to be preferred over structure II. The basic salt probably is represented best as a double salt of lead styphnate and lead hydroxide, *i.e.*, $C_6H(NO_2)_3O_2Pb \cdot Pb(OH)_2$. Such a concept receives additional support in view of the accepted structures for the basic salts of lead acetate and lead sulfate.

The well-characterized infrared spectra exhibited by normal and basic lead styphnate at frequencies below 1700 cm.$^{-1}$ undoubtedly arise from the presence of the styphnate ion. While a satisfactory interpretation of these spectra is complicated by the fact that they were obtained in the solid state, several interesting observations can be made. The infrared spectrum of styphnic acid, for example, (curve D, Fig. 1) shows a wide and broad absorption band in the 3150 cm,$^{-1}$ region, which band may be an aromatic O–H stretching frequency which would normally occur at about 3400 cm.$^{-1}$. The width of the band and the shift to a lower frequency is characteristic of strong hydrogen bonding.[14] This is not surprising, inasmuch as both hydroxyl groups in styphnic acid are ortho to two nitro groups. Hydrogen bonding is greatly enhanced under such conditions and is especially stabilized because of the large number of resonance structures[15] possible for this type of structure.

In the 1600-cm.$^{-1}$ region, where C=C stretching frequencies occur, styphnic acid possesses a well defined absorption band at 1638 cm.$^{-1}$, accompanied by a pair of bands at 1585 cm.$^{-1}$ and at 1540 cm.$^{-1}$. In the infrared spectra of *o*-nitrophenol, salicylaldehyde and phenol,[16] as well as in the spectra of other ortho substituted phenols, there is a very similar absorption in this region which quite likely is caused by vibrations of the aromatic ring. In the case of the lead salts, both of which probably contain styphnate ion, only a single, broader band, at about 1560 cm.$^{-1}$, is observed. The similarity of the spectrum of styphnic acid to that of *o*-nitrophenol and phenol itself, suggests that in the solid state the molecule is un-ionized. It was noted that recrystallized, dry styphnic acid was completely colorless and that a yellow color appeared only upon exposure to moisture. Since salts of styphnic acid containing the ion are intensely colored, and in the two cases observed possess an infrared spectrum appreciably different from that of the free acid, it appears reasonable to assume that in the dry, crystalline state, styphnic acid exists as the undissociated molecule.

Considerably more work will be required before any definite conclusion as to the structure of the lead styphnates may be drawn. Molecular weight determinations and conductivity studies would yield very valuable information. Our attempts to obtain such data were greatly hampered by the extreme insolubility of these compounds in every type of solvent used. When any solubility was found, it was accompanied by decomposition. Solubility determinations in water were carried out in this Laboratory,[17] but completely variant results were obtained. It was found that in aqueous solution, the lead styphnate undergoes hydrolysis with a resulting change in chemical species.

A complete X-ray crystal analysis would yield valuable data, but we have not succeeded in our efforts to prepare crystals of sufficient size and clarity to be useful in such a study. A more detailed investigation of the infrared spectra of these salts in the higher frequency region, with the aid of fluorite optics, might also be useful.

Acknowledgment.—Acknowledgment is made to BuORD, United States Navy, for funds in support of this work.

FAYETTEVILLE, ARKANSAS

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(12) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 78.

(13) *Ibid.*, p. 205.

(14) A. M. Buswell, V. Dietz, and W. H. Rodebush, *J. Chem. Phys.*, **5**, 501 (1937).

(15) Reference 12, pp. 318, 328.

(16) R. Barnes, U. Liddel and V. Z. Williams, *Ind. Eng. Chem., Anal. Ed.*, **14**, 877 (1942).

(17) H. Chessin, unpublished observations.