and an additional antinode in the C–C bond. The one-electron orbital jump n-π_4 gives rise to configuration II, which possesses additional nodes between the C=O and C–C bonds. Consequently, ν_1 is expected to decrease in states arising from both I and II whereas ν_2 is expected to increase in states arising from I and to decrease in states arising from II, if this simple description provides an accurate account of the changes in the π-electronic distribution in the excited states. An examination of Table IV shows that these predictions are not borne out in detail. The value of ν_1 does decrease in I^1A_u and II^1A_u, but the increase of ν_1 in I^3A_u is quite unexpected, and is difficult to explain on the basis of a simple orbital picture. Moreover, ν_2 does not increase in either I^3A_u or I^1A_u, and the observed decrease of ν_2 is contrary to the simple predictions. The naive LCAO–MO configurational description which neglects electronic repulsion and changes in the σ-bond skeleton is too crude an approximation to give an accurate account of the details of the electronic distributions.

V. Conclusions

The vibrational states of biacetyl and biacetyl-d_6 have been investigated in the ground electronic state and in three excited electronic states, and the vibrational frequencies have been compared in the different electronic states. The simple LCAO–MO description does not appear to be able to explain the changes in vibrational frequencies in the excited electronic states.

Acknowledgments.—We are extremely grateful to Professor K. S. Pitzer for several clarifying discussions. We should like to thank Professor G. C. Pimentel, Dr. E. D. Becker and Mr. R. C. Millikan for assistance with the infrared measurements. Correspondence with Dr. Tatsuo Miyazawa was also of great assistance.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

Some Divalent Metal Ethylenediammonium Phosphates; A New Series of Double Salts[1]

BY ROY C. MAST[2] AND RALPH E. OESPER

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During a systematic investigation of systems involving a divalent metal ion, ethylenediamine and ortho- or pyrophosphate ion, the following new double salts were isolated: $Mg(enH_2)(HPO_4)_2 \cdot 6H_2O$, $Mg(enH_2)(P_2O_7) \cdot 4.5H_2O$, $Zn_3(enH_2)_2(HPO_4)(PO_4)_4 \cdot 5H_2O$, $Zn_2(enH_2)(PO_4)_2$, $Zn(enH_2)_2(PO_4)_2$, $Mn_2(enH_2)(PO_4)_2 \cdot 5H_2O$, $Mn_2(enH_2)(HPO_4)_3 \cdot H_2O$, $Mn(enH_2)(P_2O_7) \cdot H_2O$, $Ni(enH_2)(HPO_4)_2 \cdot 6H_2O$, $Ni(enH_2)(P_2O_7) \cdot 4H_2O$ and $Na_2(enH_2)(P_4O_{12}) \cdot 2H_2O$. Their composition has been verified by chemical analyses. The acidity of the orthophosphate ion, when involved, has been established by an acidimetric titration. The compounds have been further characterized by their X-ray diffraction patterns.[7] One salt, a tertiary orthophosphate of magnesium and ethylenediammonium ions, was not fully characterized.

The new series of double salts described here were obtained during a detailed exploratory investigation into the chemistry of systems composed of dipositive metal ions, ortho- or pyrophosphate ions, and ethylenediamine. A wide variety of metal ammonium orthophosphates are known, and have been the subject of many studies, particularly in the field of analytical chemistry. Similarly magnesium methylammonium orthophosphate has been reported.[3] Bassett, *et al.*,[4] studies of metal(II) sodium pyrophosphates provide examples of pyrophosphate double salts and the problems encountered in studies of this sort. No double salts composed of metal(II), ethylenediamine and phosphate have been reported. In another investigation,[5] the preparation of a series of ortho- and pyrophosphates of aliphatic diamines were described. In all of the products obtained during that study, both of the basic groups of the diamine reacted. In no case was there a tendency for the diamine to appear as a monoprotic base in any of the salts isolated.

Experimental

Reagents.—Commercial ethylenediamine from Eastman Kodak Co. was distilled in an all-glass apparatus before being used. This colorless ethylenediamine was diluted to about 0.5 *M*, and the concentration of the solution determined by titration with hydrochloric acid to the methyl red end-point.

Merck "reagent grade" 85% orthophosphoric acid was diluted to about 0.5 *M*, and standardized by titration to *p*H 4.3 (*p*H meter) with sodium hydroxide solution.

Commercial crystalline pyrophosphoric acid[6] was found to be sufficiently pure for this work. The acid was stored under refrigeration (5–10°). Shortly before use, the amount needed for a reaction was dissolved in cold water and the solution, between 0.5 and 0.8 *M*, was standardized at once by titrating with sodium hydroxide to *p*H 4.3. The reaction, in which that acid was used, was carried out as rapidly as possible to the point at which precipitation commenced (at *p*H, *ca.* 2 or 3). The total elapsed time from the dissolving of the acid until a precipitate formed never exceeded 45 minutes, and the temperature never exceeded 35°. With these precautions, no serious hydrolysis to orthophosphate occurred.

Solutions of the dipositive metal ions were prepared from "reagent grade" salts which were used without further purification. Such solutions (usually 0.8 *M*) were standardized by the same analytical procedure which was later

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(1) From the Ph.D. Thesis submitted by Roy C. Mast to the Graduate School of the University of Cincinnati. Appreciation is expressed to the Procter and Gamble Company, Cincinnati, Ohio, for financial support of this work. Special acknowledgment is also due to the Laboratories of the Tanners Council of America for generously permitting the authors the unlimited use of their X-ray equipment.

(2) Address all communications to this author: The Procter and Gamble Company, Miami Valley Laboratories, Box 175, Cincinnati 31, Ohio.

(3) M. Francois, *Compt. rend.*, **146,** 1284 (1908).

(4) H. Bassett, W. L. Bedwell and J. B. Hutchinson, *J. Chem. Soc.*, 1412 (1936).

(5) R. C. Mast and R. E. Oesper, THIS JOURNAL, **77,** 6513 (1955).

(6) Provided by the Monsanto Chemical Company, Anniston, Alabama.

used to determine the metal content of the phosphates prepared from them.

Instrumental Measurements.—The *p*H measurements were made with a Beckman Model H-2 *p*H meter.

The X-ray powder patterns were obtained on a North American Phillips X-ray unit equipped with a cylindrical camera 114.6 mm. in diameter.[7] Nickel-filtered Cu Kα radiation was used. Exposure times averaged between 2 and 3 hours, and samples were mounted in finely drawn Pyrex capillaries. The accuracy of the entire procedure was checked with a pattern of pure sodium chloride.

General Procedure.—The ions involved in these systems may be brought together in a variety of ways. Reactions with both ortho- and pyrophosphate were studied in the following combinations: (1) solutions of metal ion and ethylenediammonium phosphate reacted. (2) Ethylenediamine was added to a solution containing one of four molar ratios of metal ion to phosphoric acid. These ratios were: 1:1, 2:1 and 1:2; a fourth initial condition involved ratios of metal ion to phosphoric acid to ethylenediammonium chloride of 1:1:2.

The previously described standard solutions (0.5–0.8 *M*) were used in all the reactions. These concentrations were convenient because they yielded enough precipitate for study without also producing unwieldy volumes of solution.

The reactions were carried out as quasi-titrations, *i.e.*, the reagent, usually ethylenediamine, was added in small increments accompanied by vigorous mechanical stirring. The course of each reaction was followed by continuous *p*H measurement.[7] Since the composition of the phosphate component is closely related to the hydrogen ion concentration of the solution, changes in *p*H during the course of a reaction frequently provided valuable insight into the changes undergone by this component.

As the first portions of ethylenediamine are added, only an increase in *p*H occurs. When precipitation starts, the product usually obtained contains fewer hydrogen ions associated with the phosphate than the prevailing phosphate ions in solution. Thus the formation of the solid phase liberates hydrogen ions into the solution, and therefore a change in the rate of increase of *p*H occurs, usually as a sharp inflection point. The first solid generally appears around *p*H 3–4.5, and usually contains phosphate as the monohydrogen species. As more ethylenediamine is added, a point is reached at which the precipitate reacts further, and the solid undergoes a phase transformation with the phosphate now having all hydrogens replaced. The phase change liberates more hydrogen ions into the solution with another resultant *p*H drop. There is no *p*H evidence for further phase changes, if they occur. Since the solid transformations are time consuming, 6 to 8 hours is usually required to complete such a reaction and, even then, equilibrium may not be reached in all cases.

All the different products which formed during a reaction were isolated, washed with ethyl alcohol, ethyl ether and air-dried. An X-ray powder pattern of each preparation was obtained. From these patterns, it was possible to establish the number of phases appearing in a given system. The X-ray data were supplemented by microscopic observations which revealed mixtures, especially those which contained amorphous material not detectable by X-rays.

The composition of the products was then established by chemical analysis, all determinations being carried out in duplicate. The metal, nitrogen and phosphorus content of each phase was ascertained, and a formula then deduced (if the material was not a mixture) which was complete except for water of hydration. The equivalent weight of the orthophosphate phosphorus was determined by an acidimetric titration. Finally, an attempt was made to confirm the water of hydration by heating the product to constant weight.

Analytical Procedures.—Nitrogen was determined by the Kjeldahl method, Winkler boric acid modification. Mercuric oxide was used as the catalyst in the digestion.

The phosphorus was determined in magnesium-containing compounds by precipitation as magnesium ammonium phosphate and subsequent ignition to magnesium pyrophosphate. Other divalent metal ions interfere. Consequently, in all other cases, the phosphorus was precipitated as the yellow ammonium phosphomolybdate, and subsequently ignited to phosphomolybdic oxide ($P_2O_5 \cdot 24MoO_3$).

Pyrophosphates were first hydrolyzed to orthophosphate, then the phosphorus was determined as usual.

An acidimetric titration to determine the equivalents of hydrogen in the orthophosphate ion proved quite useful. The unknown orthophosphate was dissolved in a slight excess of standard hydrochloric acid, and the excess acid back-titrated to the methyl orange end-point with sodium hydroxide. At this point a tertiary orthophosphate has consumed two equivalents of acid, while a monohydrogen orthophosphate has consumed but one. Since the percentage of phosphorus has been determined by an independent method, the data from the acidimetric titration may be used to calculate the equivalent weight of the phosphorus, and thereby establish the acidity of the orthophosphate.

Thus a completely substituted orthophosphate reacts with two equivalents of acid giving the phosphorus an equivalent weight of 15.5; a monohydrogen orthophosphate consumes one equivalent of acid giving an equivalent weight of 31 for the phosphorus. If no acid is consumed, the material is a dihydrogen orthophosphate. Intermediate figures indicate a mixture of acid orthophosphate ions in the preparation. This titration was not used with pyrophosphates because the products were either involved mixtures or straightforward compounds with the phosphate as $P_2O_7^{-4}$.

Magnesium was precipitated as magnesium ammonium phosphate and subsequently ignited at 1000° to magnesium pyrophosphate.

Zinc was determined by precipitation with 8-hydroxyquinoline and drying to constant weight at 130°.

Manganese was precipitated as manganous ammonium phosphate, then ignited to manganous pyrophosphate at 950–1000°.

Nickel was weighed as the familiar dimethylglyoximate dried to constant weight at 110°.

Magnesium Ethylenediammonium Phosphates

$Mg(enH_2)(HPO_4)_2 \cdot 6H_2O$.—A white crystalline material having this composition appears over a wide range of conditions. It is the only product which precipitates when solutions of ethylenediammonium orthophosphate and magnesium chloride are brought together. It appears at *p*H 4.6–4.8 when ethylenediamine is added to each of the four initial mixtures, and remains unchanged in all four cases until *p*H 8.0–8.2 is reached.

Anal. Calcd. for $Mg(enH_2)(HPO_4)_2 \cdot 6H_2O$: Mg, 6.25; N, 7.25; P, 15.97; H_2O, 27.95. Found: Mg, 6.33; N, 7.28; P, 15.92; H_2O (125°), 27.75; equiv. wt. of phosphorus, 30.9, indicating monohydrogen orthophosphate. Microscopic examination showed that the crystals were perfect rectangular prisms.

Tertiary Double Salt.—Above *p*H 8.0–8.2, $Mg(enH_2)(HPO_4)_2 \cdot 6H_2O$ changes to a new product. If excess magnesium ions are present, $Mg_3(PO_4)_2 \cdot 8H_2O$ forms. If either the phosphate or ethylenediammonium ions are in excess, a more complex material forms. Its X-ray powder pattern differs from that of either $Mg_3(PO_4)_2 \cdot 8H_2O$ or $Mg(enH_2)(HPO_4)_2 \cdot 6H_2O$. The same phase can also be obtained in the presence of excess magnesium ions from solutions at very high *p*H (*ca.* 12). All preparations giving this particular X-ray pattern had constant composition. All the analytical evidence seems to indicate a non-stoichiometric tertiary orthophosphate. The percentages found were: N, 6.97; P, 17.73; and Mg, 14.41, which correspond to 1.2 Mg, 1.0 N, and 1.1 P; a satisfactory cation–anion balance of 2.94:3.00 equivalents. The equivalent weight of phosphorus is 15.6. This phase does approach the composition $Mg_2(enH_2)(PO_4)_2 \cdot 3H_2O$ whose theoretical composition is N 7.90%, P 17.45%, and Mg 13.71%.

$Mg(enH_2)(P_2O_7) \cdot 4.5H_2O$.—A solid which has this composition appears between *p*H 3.6–3.8 when ethylenediamine is added to a solution which contains equimolar amounts of pyrophosphoric acid and magnesium ions, excess pyrophosphate, or excess ethylenediammonium ions. It undergoes no changes even when the *p*H is raised to 10 by adding ethylenediamine.

Anal. Calcd. for $Mg(enH_2)(P_2O_7) \cdot 4.5H_2O$: Mg, 7.14; N, 8.21; P, 18.13; H_2O, 23.81. Found: Mg, 7.10; N,

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(7) An accompanying figure and the tables of X-ray powder patterns have been deposited as Document number 4664 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

8.08; P, 18.15 and H_2O (115°), 23.92. The crystals appear (×450) as very small, closely packed spherulites.

Other Pyrophosphates.—Mixtures result when solutions of ethylenediammonium pyrophosphate and magnesium chloride react, or when ethylenediamine is added to a pyrophosphoric acid solution containing excess magnesium ions. The products are very finely divided, the entire preparation frequently assuming the consistency of a rather viscous hydrous gel. The X-ray patterns of these preparations are diffuse, and show no more than a few weak, poorly defined lines. The analytical data indicate that much of the product is magnesium pyrophosphate.

Zinc Ethylenediammonium Phosphates

$Zn_2(enH_2)(PO_4)_2$.—This is the most common product in the zinc–ethylenediammonium–orthophosphate system. It forms when zinc sulfate and ethylenediammonium orthophosphate solutions are brought together, and it also appears at some time during each of the four reactions with extended *p*H range, in which ethylenediamine is added to a zinc sulfate–phosphoric acid solution. When the initial molar ratio of $ZnSO_4:H_3PO_4$ is 1:1, $Zn_2(enH_2)(PO_4)_2$ forms during a phase transformation which occurs at *p*H 4.3. With zinc ions in excess, the double salt forms from $Zn_3(PO_4)_2\cdot 4H_2O$ at *p*H 7.5. It is the initial precipitate (at *p*H 2.5) when excess ethylenediammonium ion is present, and it becomes the only solid in suspension at *p*H 3.6 in a solution containing excess orthophosphate ions. Once formed, it remains unchanged during the subsequent course of the reaction.

Anal. Calcd. for $Zn_2(enH_2)(PO_4)_2$: Zn, 34.18; N, 7.31; P, 16.15. Found: Zn, 34.26; N, 7.38; P, 16.06; equiv. wt. of phosphorus, 15.5. The product loses no weight at 160°. When magnified 450×, the dense crystals are minute, colorless tablets.

$Zn_5(enH_2)_2(HPO_4)(PO_4)_4\cdot 5H_2O$; $(ZnHPO_4\cdot 2Zn_2(enH_2)(PO_4)_2\cdot 5H_2O)$.—A solid which has this composition can be obtained by adding 0.5 *M* ethylenediamine to a solution containing 0.8 *M* zinc sulfate, 0.5 *M* orthophosphoric acid and 30 mmoles of ethylenediammonium hydrochloride in an initial molar ratio of 2:1:2. The reaction is stopped at *p*H 2.7, and the crystals separated by filtration.

Anal. Calcd. for $Zn_5(enH_2)_2(HPO_4)(PO_4)_4\cdot 5H_2O$: Zn, 32.15; N, 5.51; P, 15.30. Found: Zn, 31.84; N, 5.54; P, 15.31. The equivalent weight of phosphorus is 18.7. Since this value falls between 15.5 (for PO_4^{-3}) and 31.0 (for HPO_4^{-2}), it is logical to assume that both of these orthophosphate species are present. Applying standard analytical calculations, the ratio of tertiary orthophosphate to monohydrogen orthophosphate is 4:1.[8] These colorless crystals are uniformly acicular when examined microscopically. The compound did not reach constant weight when heated.

$Zn(enH_2)_2(PO_4)_2$.—This product was obtained by mixing 2.9 g. of $Zn_2(enH_2)(PO_4)_2$ with 50 ml. of 40% ethylenediamine. The starting material does not dissolve immediately. After the mixture has been stirred for 15 minutes, the original tablets of $Zn_2(enH_2)(PO_4)_2$ change to short rectangular prisms of the new substance.

Anal. Calcd. for $Zn(enH_2)_2(PO_4)_2$: Zn, 17.22; N, 14.75; P, 16.32. Found: Zn, 17.20; N, 14.59; P, 16.17; equiv. wt. of phosphorus, 15.3.

If the mixture is stirred over a more extended period of time (2–3 hours) the expected behavior occurs, and the solid dissolves, presumably forming a zinc–ethylenediamine complex ion.

Zinc Ethylenediamine Pyrophosphate Studies.—An extensive series of reactions involving zinc, ethylenediammonium and pyrophosphate ions was carried out. However, all resulted in mixtures, usually composed of $Zn_2P_2O_7\cdot 5H_2O$ and some other constituent, presumably some zinc ethylenediammonium pyrophosphate. The presence of the zinc pyrophosphate was established by X-ray patterns.[9]

Manganous Ethylenediammonium Phosphates

$Mn_2(enH_2)(PO_4)_2\cdot 5H_2O$.—This compound was obtained in two of the reactions. When ethylenediamine is added to a solution containing orthophosphoric acid and manganous sulfate in an initial 1:1 molar ratio, a homogeneous solid of the composition $Mn_2(enH_2)(PO_4)_2\cdot 5H_2O$ appears at *p*H 6.6. It remains unchanged until *p*H 8.0 is reached, and there an amorphous solid also appears. $Mn_2(enH_2)(PO_4)_2\cdot 5H_2O$ is also the solid phase which forms at *p*H 6.5 when ethylenediamine is added to a solution which originally contains excess orthophosphoric acid (starting ratio of $H_3PO_4:MnSO_4$ is 2:1).

Anal. Calcd. for $Mn_2(enH_2)(PO_4)_2\cdot 5H_2O$: Mn, 24.41; N, 6.22; P, 13.77; H_2O, 20.00. Found: Mn, 24.34; N, 6.11; P, 13.75; H_2O, 19.84 (135°); equiv. wt. of the phosphorus, 15.4. The crystals are very small rectangular prisms, light pink in color.

$Mn_2(enH_2)(HPO_4)_3\cdot H_2O$.—A solid phase having this composition was obtained under only one set of conditions. It is the crystalline solid which forms from $MnHPO_4\cdot 3H_2O$ at *p*H 4.6 when ethylenediamine is added to a solution which originally contains excess orthophosphoric acid. (Initial molar ratio of $H_3PO_4:MnSO_4 = 2:1$.) There is no further change until *p*H 6.5 is reached, when $Mn_2(enH_2)(HPO_4)_3\cdot H_2O$ changes to $Mn_2(enH_2)(PO_4)_2\cdot 5H_2O$.

Anal. Calcd. for $Mn_2(enH_2)(HPO_4)_3\cdot H_2O$: Mn, 22.95; N, 5.96; P, 19.43; H_2O, 3.77. Found: Mn, 22.83; N, 5.95; P, 19.40; H_2O, 3.85 (135°); equiv. wt. of phosphorus, 30.7. The pink crystals are bladed, somewhat acicular in appearance.

Pure compounds were obtained from the manganous–ethylenediamine–orthophosphate system under the conditions just described. Generally, precipitation starts at about *p*H 3.5, but that solid is usually a mixture. Above *p*H 8.5 or 9, amorphous manganous hydroxide appears, and rapidly oxidizes to brown hydrated oxides of higher valence states of manganese.

$Mn(enH_2)(P_2O_7)\cdot H_2O$.—When ethylenediamine is added to a solution which contains pyrophosphoric acid and manganous sulfate in any of the starting ratios, precipitation begins at *p*H 1.7. This solid is a nondescript mixture. In all cases, except the solution which contained excess manganous ions, a phase transformation occurs about *p*H 4. The resulting product, $Mn(enH_2)(P_2O_7)\cdot H_2O$, remains unchanged until *p*H 8.5 or 9 is reached—where the brown coloration again develops.

Anal. Calcd. for $Mn(enH_2)(P_2O_7)\cdot H_2O$: Mn, 17.75; N, 9.06; P, 20.05; H_2O, 5.83. Found: Mn, 17.54; N, 9.14; P, 19.95.

The product is quite stable to heat and could not be successfully dehydrated. It loses water slowly, but fails to reach constant weight, even at 155°. At this temperature, it has lost only 3.5% of its weight. The crystals may vary in appearance from extremely minute, light pink (nearly white) crystals, so small that they appear to be circular even when magnified 450 times, up to somewhat larger (but still very small) closely packed spherulites.

No single pure phase was isolated from the reaction in which ethylenediamine was added to a solution which contained pyrophosphoric acid and excess manganous sulfate (initial molar ratio $MnSO_4:H_4P_2O_7 = 2:1$).

Nickel Ethylenediammonium Phosphates

$Ni(enH_2)(HPO_4)_2\cdot 6H_2O$.—When nickel is added to a solution of ethylenediammonium orthophosphate, a soluble complex forms, and a violet coloration develops. As the addition is continued, and the falling *p*H reaches 6.1, precipitation of $Ni(enH_2)(HPO_4)_2\cdot 6H_2O$ starts. This compound also forms when ethylenediamine is added to a solution initially containing nickel sulfate and orthophosphoric acid. The precipitate first formed at *p*H 4.5 is amorphous to X-rays. At *p*H 4.7, it undergoes a phase change which yields $Ni(enH_2)(HPO_4)_2\cdot 6H_2O$. As still more ethylenediamine is added, this precipitate begins to dissolve at *p*H 5.9.

Anal. Calcd. for $Ni(enH_2)(HPO_4)_2\cdot 6H_2O$: Ni, 13.95; N, 6.65; P, 14.73; H_2O, 25.65. Found: Ni, 13.92; N, 6.67; P, 14.55; H_2O, 25.52 (130°); equiv. wt. of phosphorus, 31.1. The crystals are pale green prisms.

$Ni(enH_2)(P_2O_7)\cdot 4H_2O$.—When ethylenediamine is added to 1:1 solution of nickel sulfate and pyrophosphoric acid, an amorphous (to X-rays) precipitate forms at *p*H 3.2. At *p*H 6.1, the solid transforms to a crystalline material having the composition $Ni(enH_2)(P_2O_7)\cdot 4H_2O$. If the reaction is continued to much higher *p*H values, the precipitate dis-

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[8] The literature contains reports of analogous double orthophosphates, involving two stages of neutralization of the orthophosphate, *e.g.*, see the review by B. Wendrow and K. A. Kobe, *Chem. Revs.*, **54**, 891 (1954).

[9] O. T. Quimby and H. W. McCune, unpublished results.

solves, forming a violet colored solution of soluble complexes. The $Ni(enH_2)(P_2O_7)\cdot 4H_2O$ can be reprecipitated by adding dilute hydrochloric acid until all of the violet, then blue color is discharged.

Anal. Calcd. for $Ni(enH_2)(P_2O_7)\cdot 4H_2O$: Ni, 15.98; N, 7.63; P, 16.90; H_2O, 19.62. Found: Ni, 15.88; N, 7.58; P, 17.10; H_2O (145°), 19.77. The apple green crystals were obtained in the form of prismatic spherulites.

A Tetrametaphosphate

$Na_2(enH_2)(P_4O_{12})\cdot 2H_2O$.—Brief, exploratory reactions were carried out with the various divalent metal ions, ethylenediamine and several condensed phosphates. Most such reactions led to mixtures, or to salts that have been reported by previous workers. However, when the condensed phosphate was sodium tetrametaphosphate, one single product was consistently obtained. Reactions were performed by dropping dilute hydrochloric acid into a solution of the metal ion (0.8 *M*), until the *p*H reached 1.0 or less. A quantity of sodium tetrametaphosphate equimolar to the amount of metal salt present was then added, and ethylenediamine added slowly. A precipitate appears, and remains unchanged until the *p*H is raised to at least 6.0.

Anal. Calcd. for $Na_2(enH_2)(P_4O_{12})\cdot 2H_2O$: P, 27.10; N, 6.09. Found: P, 27.07; N, 6.04.

These prismatic crystals lose no weight at 105°. Dehydration of condensed phosphates by heat above this temperature are of questionable analytical value because hydrolysis of the phosphate by the water of hydration is quite possible.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LAVAL UNIVERSITY]

Recommended Values for the Thermodynamic Properties of Hydrogen and Deuterium Peroxides[1]

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Recent spectroscopic and calorimetric data on H_2O_2 have been used to recalculate the thermodynamic functions of that compound. The contribution of the internal rotation mode was estimated using an equivalent potential barrier height of 4.45 kcal. based on the third law entropy. Similar calculations were carried out for the isotopic molecules D_2O_2 and HDO_2. Various derived thermodynamic quantities of the peroxide molecules are tabulated for convenience. From these the dissociation energy D(HO–OH) is found to be 51 kcal. at 0°K.

A few years ago one of us calculated the thermodynamic functions for hydrogen peroxide and some of its most important reactions.[2] Since then new spectroscopic[3] and calorimeteric measurements[4,5] have been reported which justify revision of these quantities of fundamental interest. The major uncertainty in the previous values arose from the internal rotation mode about which little definite information was then available. Thanks to the recent determination of the calorimetric entropy[4] the uncertainty has now been reduced significantly. This was confirmed by treating the internal rotation by an alternate method, which gave very nearly the same values of the thermodynamic quantities for all temperatures up to 1500°K. Further improvements in the accuracy of these data will have to await more complete knowledge of the height and shape of the potential barriers restricting mutual rotation of the OH groups. Also, because the peroxide molecule is not a very rigid one, such terms as anharmonicity of vibrations and centrifugal stretching may become significant at high temperatures.

The same structural parameters were assumed for the three isotopic molecules,[3] namely: $r_{O-H} = r_{O-D} = 0.965$ Å.; $r_{O-O} = 1.49$ Å.; $\alpha_{OOH} = \alpha_{OOD} = 100°$; $\phi = 95°$. The calculated moments of inertia and the vibrational frequencies are listed in Table I. Obviously those for the hybrid molecule HDO_2 are less accurately known than for the other two. The external symmetry number of that molecule is only 1, and the reduced moment for internal rotation is given with sufficient accuracy by the expression

$$I_{\text{red.}} = \frac{I_A \times I_A'}{2(I_A + I_A')} \tag{1}$$

where I_A and I_A' are the small moments of inertia of H_2O_2 and D_2O_2, respectively.

TABLE I

MOLECULAR DATA FOR THE THREE ISOTOPIC PEROXIDES

Vibrational frequencies, cm.$^{-1}$

	H_2O_2	D_2O_2		HDO_2
ν_1	3610	2660	ν_{OH}	3610
ν_2	1350	1015	ν_{OD}	2660
ν_3	880	880	δ_{OH}	1310
ν_4	520	400 (?)	δ_{OD}	980
ν_5	3610	2660	ν_{OO}	880
ν_6	1266	947	δ_{torsion}	450 (?)

Moments of inertia (in 10^{-40} g. cm.^{2})

	H_2O_2	D_2O_2	HDO_2
I_A	2.785	5.14	3.98
I_B	34.0	38.3	35.9
I_C	33.8	37.9	36.6
$I_{\text{red.}}$	0.696	1.29	0.90

The question of internal rotation was dealt with by the method of Pitzer[6] for unsymmetrical tops attached to a rigid frame. According to that treatment the OH group is classified among those with a relatively small "off balance" factor. Such simplification is justified in the case of H_2O_2 (and to a slightly lesser extent for D_2O_2) as confirmed by the moderate change in the over-all moments of inertia with internal rotation.[7] Although the potential

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[1] This work was supported by the U. S. Air Force, through the Office of Scientific Research of the Air Research Development Command.

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