

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

## Electronic and Vibrational States of Biacetyl and Biacetyl- $d_6$ . II. Vibrational States<sup>1</sup>

BY JEROME W. SIDMAN<sup>2</sup> AND DONALD S. MCCLURE

RECEIVED AUGUST 18, 1955

The infrared absorption spectrum of biacetyl has been measured from 140 to 4000  $\text{cm}^{-1}$ . The electronic-vibrational transitions of biacetyl have been vibrationally analyzed, and vibrational assignments for biacetyl and biacetyl- $d_6$  are proposed for the ground state and three excited electronic states. A comparison of vibrational frequencies in the various electronic states indicates that the simple LCAO-MO theory is not sufficiently exact to predict the direction of change of a vibrational frequency in excited electronic states.

### I. Introduction

The infrared spectrum of biacetyl has recently been measured by Miyazawa,<sup>3</sup> who has also performed a normal coordinate analysis of the skeletal vibrations of biacetyl.<sup>4</sup> In this paper, the infrared spectrum of biacetyl- $d_6$  is compared with that of biacetyl, and the interpretations and predictions of Miyazawa are verified in several respects. In addition to the methods of infrared and Raman spectroscopy for studying the vibrational frequencies of molecules in the ground electronic state, the vibrational analysis of electronic-vibrational emission transitions can also be used. Analyses of absorption transitions can be used to obtain information about vibrational frequencies in excited electronic states. Vibrational analyses of the electronic-vibrational transitions of biacetyl under conditions of high resolution have been described in paper I,<sup>5</sup> so that vibrational frequencies are known in three excited electronic states, in addition to the ground electronic state. Assignments will now be proposed for the vibrations of biacetyl and biacetyl- $d_6$  in the excited and ground electronic states. The change in frequency of the same vibrational mode in different electronic states gives qualitative information about the electronic distribution in excited states, and these results can be used to check the predictions of the LCAO-MO theory.

### II. Experimental

The biacetyl and biacetyl- $d_6$  were prepared and purified as discussed in paper I. The infrared absorption spectra of biacetyl and biacetyl- $d_6$  were measured in the liquid and vapor states from 670 to 4000  $\text{cm}^{-1}$  on the Perkin-Elmer Model 21 double-beam spectrophotometer using a NaCl prism, and from 360 to 670  $\text{cm}^{-1}$  on the Perkin-Elmer Model 12C spectrophotometer, using a KBr prism. The infrared absorption spectrum of biacetyl was measured in the vapor state from 140 to 420  $\text{cm}^{-1}$  on a vacuum grating spectrometer.<sup>6</sup>

The measurement and analysis of the electronic-vibrational emission and absorption spectra have been discussed in paper I.

(1) (a) This work was partially supported by the U. S. Office of Naval Research under Contract N6 ori-211-T.O.III. A preliminary report of the work was presented at the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society in New York City, September, 1954. (b) From the dissertation submitted by Jerome W. Sidman to the Graduate Faculty of the University of California, June, 1955, in partial fulfillment of the requirements for the Ph.D. degree.

(2) Du Pont Teaching Fellow, 1954-1955.

(3) T. Miyazawa, *J. Chem. Soc. Japan*, **74**, 743 (1953).

(4) T. Miyazawa, *ibid.*, **74**, 915 (1953).

(5) J. W. Sidman and D. S. McClure, *THIS JOURNAL*, **77**, 6461 (1955).

(6) C. R. Bohn, N. K. Freeman, W. D. Gwinn, J. L. Hollenberg and K. S. Pitzer, *J. Chem. Phys.*, **21**, 719 (1953).

### III. Results

The observed infrared absorption maxima of biacetyl and biacetyl- $d_6$  are listed with analyses in Tables I and II, and the spectra are shown in Figs. 1 and 2.

The assignments of the vibrational fundamentals in the ground electronic state and in the excited electronic states are listed in Tables III and IV, and a discussion of the assignments will now be given.

TABLE I  
INFRARED ABSORPTION OF  $\text{Ac}_2$

$\nu$ ( $\text{cm}^{-1}$ ) and intensity		Assignment
Liquid	Vapor	
..	257 s	Skeletal bending, $b_u$
..	347 m	Out-of-plane skeletal bending, $a_u$
538 s	539 s	Skeletal bending, $b_u$
915 m	915 m	380, $a_g$ + 539, $b_u$ } Fermi resonance
950 m	945 m	
1118 s	1115 s	CH <sub>3</sub> rocking, $b_u$ or $a_u$
1355 s	1360 s	CH <sub>3</sub> symm. bending, $b_u$
1425 m	1430 m	CH <sub>3</sub> asymm. bending, $b_u$ or $a_u$
1714 vs	1725 vs	C=O stretching, $b_u$ } Fermi resonance
1721 vs	1735 vs	
2930 w	2930 w	CH <sub>3</sub> symm. stretching, $b_u$
3010 w	3000 w	CH <sub>3</sub> asymm. stretching, $b_u$ or $a_u$
3430 w	3430 w	1720, $b_u$ + 1730, $a_g$
3520 w	Absent	
3650 w	Absent	

TABLE II

INFRARED ABSORPTION OF  $\text{Ac}_2-d_6$

$\nu$ ( $\text{cm}^{-1}$ ) and intensity		Assignment
Liquid	Vapor	
476 s	476 s	Skeletal bending, $b_u$
777 m	770 vw	C-CD <sub>3</sub> stretching, $b_u$
962 s	962 m	CD <sub>3</sub> rocking, $a_u$ or $b_u$
1027 m	1038 w	CD <sub>3</sub> symmetric bending, $b_u$
1114 m	1115 m	CD <sub>3</sub> asymmetric bending, $b_u$ or $a_u$
1140 vs	1135 vs	CD <sub>3</sub> asymmetric bending, $a_u$ or $b_u$
1234 w	1240 w	CHD <sub>2</sub> bending, isotopic impurity
1254 w	1260 w	CHD <sub>2</sub> bending, isotopic impurity
1290 w	1290 w	CHD <sub>2</sub> bending, isotopic impurity
1712 vs	1722 vs	C=O stretching, $b_u$
2140 w	2150 vvw	CD <sub>3</sub> symm. stretching, $b_u$
2270 w	2280 vvw	CD <sub>3</sub> asymm. stretching, $b_u$ or $a_u$
2450 w	?	CHD <sub>2</sub> stretching, isotopic impurity
3010 vw	3000 vvw	CHD <sub>2</sub> stretching, isotopic impurity
3034 w	3430 w	1720, $b_u$ + 1730, $a_g$
3700 w	Absent	

### IV. Interpretation of the Spectra

**A. The Ground Electronic State.**—The infrared spectra of biacetyl in the region 360 to 4000

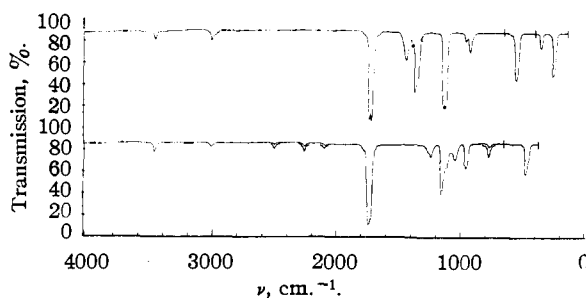


Fig. 1.—Top curve, infrared absorption spectrum of biacetyl vapor;  $T = 300^\circ\text{K}$ . Intensities in the region  $140\text{--}420\text{ cm.}^{-1}$  may be uncertain by 50%, due to stray light; pressure =  $10\text{--}30\text{ mm.}$  (in region  $420\text{--}4000\text{ cm.}^{-1}$ ); path length =  $7\text{ cm.}$  (in region  $420\text{--}4000\text{ cm.}^{-1}$ ).

Fig. 2.—Bottom curve, infrared absorption spectrum of biacetyl- $d_6$  vapor,  $T = 300^\circ\text{K}$ .; pressure =  $10\text{--}30\text{ mm.}$ ; path length  $7\text{ cm.}$

TABLE III

Motion	VIBRATIONAL ASSIGNMENTS OF $\text{Ac}_2$ AND $\text{Ac}_2\text{-}d_6$ IN ${}^1\text{A}_g$	
	$\text{Ac}_2\text{-}h_s$	$\text{Ac}_2\text{-}d_6$
$\nu_1$ , C=O stretch, $a_g$	1729	1728
$\nu_2$ , C-C stretch, $a_g$	1284	1300
$\nu_3$ , C-methyl stretch, $a_g$	1056	953
$\nu_4$ , skeletal bend, $a_g$	617	
$\nu_5$ , skeletal bend, $a_g$	380	344
$\nu_6$ , C=O stretch, $b_u$	1730 (1355 + 380)	1722
$\nu_7$ , C-methyl stretch, $b_u$	945 (538 + 380)	770
$\nu_8$ , skeletal bend, $b_u$	538	476
$\nu_9$ , skeletal bend, $b_u$	257	
$\nu_{10}$ , acetyl torsion, $a_u$	<140 (35?)	(35?)
$\nu_{11}$ , out-of-plane bend, $a_u$	347	
$\nu_{12}$ , out-of plane bend, $b_g$	550 <sup>a</sup>	
Methyl rocking, $a_u$ or $b_u$	1115	962
Symm. methyl bending, $b_u$	1360	1038
Asymm. methyl bending, $b_u$ or $a_u$	1430	1115, 1135
Symm. methyl stretching, $b_u$	2930	2150
Asymm. methyl stretching, $b_u$ or $a_u$	3000	2280

TABLE IV

Vibrational mode	VIBRATIONAL CORRELATIONS IN VARIOUS ELECTRONIC STATES									
	$\text{Ac}_2\text{-}h_s$	$X^1\text{A}_g$	$\text{Ac}_2\text{-}d_6$	Electronic state $I^1\text{A}_u$			$I^1\text{A}_u$	$\text{Ac}_2\text{-}d_6$	$II^1\text{A}_u$	
				$\text{Ac}_2\text{-}h_s$	$\text{Ac}_2\text{-}d_6$	$\text{Ac}_2\text{-}h_s$		$\text{Ac}_2\text{-}d_6$	$\text{Ac}_2\text{-}h_s$	$\text{Ac}_2\text{-}d_6$
$\nu_1$ , C=O stretch, $a_g$	1729		1728	1751	1749	1447		1424	1547	1523
$\nu_2$ , C-C stretch, $a_g$	1284		1300	1144	1148	1136		1141		
$\nu_3$ , C-methyl stretch, $a_g$	1056		953	1009	825	998		823	982	777
$\nu_4$ , skeletal bend, $a_g$	617					495		464		
$\nu_5$ , skeletal bend, $a_g$	380		344	358	325	356		321	348	325
$\nu_{10}$ , acetyl torsion, $a_u$	<140 (35?)		<140 (35?)	35?	35?	95 (35?)		96 (35?)	82 (36?)	87 (40?)
Methyl stretching, $a_g$	~3000		~2100			2971		~2100		
Symm. methyl bending, $a_g$	~1360		~1030						1355	1156
Asymm. methyl bending, $a_g$	~1430		~1130	1469						

NOTE: Values marked ~ are estimated from the corresponding motions of the  $b_u$  class in  $X^1\text{A}_g$ . The uncertainty in most of the frequencies is approximately  $6\text{ cm.}^{-1}$ . The frequencies in  $II^1\text{A}_u$  may be uncertain by  $10\text{ cm.}^{-1}$ . The  $35\text{ cm.}^{-1}$  frequency represents the average of many intervals, and is considered accurate to  $2\text{ cm.}^{-1}$ .

$\text{cm.}^{-1}$  agree within limits of error with the spectra reported by Miyazawa.<sup>3</sup> The measurement of the far infrared spectrum of biacetyl has revealed two additional absorption bands, at  $257\text{ cm.}^{-1}$  and at  $347\text{ cm.}^{-1}$ . The absorption at  $257\text{ cm.}^{-1}$  is assigned

to a  $b_u$  skeletal bending motion which has been predicted by Miyazawa from a normal coordinate analysis of biacetyl.<sup>4</sup> The absorption band at  $347\text{ cm.}^{-1}$  is assigned to an out-of-plane  $a_u$  skeletal bending motion.

The infrared spectrum of biacetyl- $d_6$  confirms many of the interpretations of Miyazawa.<sup>3</sup> The bands at  $915$  and  $945\text{ cm.}^{-1}$  in  $\text{Ac}_2$  are assigned by Miyazawa to Fermi resonance of a  $b_u$  C- $\text{CH}_3$  stretching fundamental with a combination band,  $539, b_u + 380, a_g$ . In agreement with this assignment, only one absorption band is found in  $\text{Ac}_2\text{-}d_6$  at  $770\text{ cm.}^{-1}$ . Miyazawa had previously suggested that the C- $\text{CH}_3$  stretching modes of biacetyl in the region  $900\text{--}1100\text{ cm.}^{-1}$  might be expected to mix with the appropriate  $\text{CH}_3$  rocking modes with similar frequency.<sup>3</sup> The decrease of 23% for the frequency in  $\text{Ac}_2\text{-}d_6$  of the  $b_u$  C- $\text{CD}_3$  stretching mode in the ground electronic state does indicate that hydrogenic vibrations are mixed with the  $b_u$  C- $\text{CH}_3$  stretching mode. Furthermore, the  $a_g$  C- $\text{CH}_3$  stretching modes in the excited electronic states also exhibit frequency shifts of approximately 20% with deuteration, indicating that the skeletal approximation is a poor one for this vibration, in agreement with Miyazawa's predictions.

The decrease in frequency of the normal vibrational modes of biacetyl with deuteration is quite similar to the corresponding frequency decrease of the vibrational modes of acetaldehyde with deuteration,<sup>7</sup> insofar as the molecules can be compared. The weak infrared absorption bands at  $1240, 1260$  and  $1290\text{ cm.}^{-1}$  in  $\text{Ac}_2\text{-}d_6$  are assigned to  $\text{CHD}_2$  bending motions of the  $\text{Ac}_2\text{-}d_6h$  isotropic impurity, which is present in 16% concentration in the  $\text{Ac}_2\text{-}d_6$  sample used in these measurements. These bands are relatively more intense in samples of  $\text{Ac}_2\text{-}d_6$  which contain less deuterium.

The vibrational frequencies of biacetyl in the  ${}^1\text{A}_g$  state deduced from the vibrational analyses of the crystal emission spectra are in fairly good agreement with the results of the Raman spectra as investigated by Kohlrausch and Pongratz<sup>8</sup> and by Miyazawa.<sup>9</sup> The upward shift of the  $1280\text{ cm.}^{-1}$

interval (assigned to an  $a_g$  C-C stretching funda-

(7) J. C. Morris, *J. Chem. Phys.*, **11**, 230 (1943).

(8) K. W. F. Kohlrausch and E. Pongratz, *Ber.*, **67B**, 985 (1934).

(9) T. Miyazawa, private communication. We are grateful to Dr. Miyazawa for permission to quote from his results.

mental) to  $1300\text{ cm.}^{-1}$  in  $\text{Ac}_2-d_6$  is probably due to the fact that the  $a_g$   $\text{CH}_3$  bending motions in  $\text{Ac}_2$  in the range  $1300\text{--}1500\text{ cm.}^{-1}$  are at higher frequencies than the  $a_g$  C-C stretching mode, whereas the  $a_g$   $\text{CD}_3$  bending motions in  $\text{Ac}_2-d_6$  in the range  $1000\text{--}1200\text{ cm.}^{-1}$  are at lower frequencies other than the  $a_g$  C-C stretching mode. Thus, the interactions between  $\text{CH}_3$  or  $\text{CD}_3$  bending and C-C stretching cause the latter vibrational frequency to move down in  $\text{Ac}_2$  and up in  $\text{Ac}_2-d_6$ .<sup>10</sup>

The infrared absorption spectrum of  $\text{Ac}_2$  vapor shows two peaks in the C=O stretching region, whereas only one is seen with certainty in  $\text{Ac}_2-d_6$ . Only one of the two C=O stretching modes is infrared active for the  $\text{C}_{2v}$  model of biacetyl, so that the presence of the two peaks in  $\text{Ac}_2$  is best attributed to Fermi resonance of the  $b_u$  C=O stretch with the combination  $1355, b_u + 380, a_g$ .

There appears to be no evidence for the existence of rotational isomers of biacetyl at room temperatures. The infrared spectra of biacetyl at  $470^\circ\text{K}$ . do not show the presence of any absorption maxima which are not present at room temperature. Furthermore, none of the infrared vapor bands disappear or weaken greatly in the infrared absorption spectrum of solid biacetyl at  $190^\circ\text{K}$ .<sup>9</sup> This is additional evidence that only one molecular form of biacetyl is present in any detectable concentration at room temperature.

The  $a_g$  C-C stretching frequency in biacetyl,  $\nu_2$ , is  $1280\text{--}1300\text{ cm.}^{-1}$ . The corresponding frequency in glyoxal is  $1207\text{ cm.}^{-1}$ ,<sup>11</sup> whereas the corresponding frequency in 1,3-butadiene is  $1205\text{ cm.}^{-1}$ .<sup>12</sup> This is rather high for a C-C stretching motion, and is attributed to the partial double bond character of the central C-C bond, which is  $1.46\text{--}1.47\text{ \AA}$ . in length in glyoxal and biacetyl,<sup>13</sup> and which is therefore considerably shorter than the "normal" C-C single bond length of  $1.53\text{--}1.54\text{ \AA}$ .

The prominence of the  $35\text{ cm.}^{-1}$  interval in the electronic-vibrational spectra of  $\text{Ac}_2$  and  $\text{Ac}_2-d_6$  is unexpected. Since the progressions of the  $35\text{ cm.}^{-1}$  interval show an alternation of intensities, this interval must be due to a non-totally symmetric vibration of biacetyl in the crystalline state. The only molecular vibration expected to have a very low frequency and a very small deuteration shift is the acetyl torsion. This motion has not been located in the infrared spectrum down to  $140\text{ cm.}^{-1}$ . The corresponding  $a_u$  formyl torsion in glyoxal has been assigned the value  $127\text{ cm.}^{-1}$  ( $117\text{ cm.}^{-1}$  in  $(\text{CDO})_2$ ),<sup>11</sup> and the corresponding  $a_u$  torsion in 1,3-butadiene has been assigned the value  $170\text{ cm.}^{-1}$ ,<sup>12</sup> so that  $35\text{ cm.}^{-1}$  is much lower than is expected for this torsional motion in biacetyl. If the interval does not correspond to an internal motion of biacetyl, then it must be assigned to a non-totally symmetric lattice mode of the biacetyl crystal.

The complex, almost diffuse appearance of the

(10) We are grateful to Prof. K. S. Pitzer for suggesting this interpretation of the anomalous shift.

(11) J. C. D. Brand, *Trans. Faraday Soc.*, **50**, 431 (1954).

(12) R. E. Richards and J. R. Nielsen, *J. Opt. Sci. Amer.*, **40**, 438 (1950).

(13) J. E. LuValle and V. Schomaker, *This Journal*, **61**, 3520 (1939).

${}^1A_u \leftarrow {}^1A_g$  absorption transition in the vapor is due both to the presence of low frequency vibrations of biacetyl and to unresolved rotational structure, since the same transition in glyoxal is quite sharp in the vapor. The methyl groups in biacetyl introduce low frequency methyl torsional vibrational levels which are thermally populated at room temperature. Absorption by these vibrationally excited molecules gives the spectrum a complex appearance. The spectrum of the crystal at  $20^\circ\text{K}$ . is sharper because rotational structure is removed and excited vibrational and lattice states are not populated.

The assignments of the fundamental vibrational frequencies of biacetyl in the ground electronic state as given in Table III are based on the results of the infrared spectra, the Raman spectra and the crystal emission spectra.

**B. The Excited Electronic States.**—Since the crystal absorption spectra of both  $\text{Ac}_2$  and  $\text{Ac}_2-d_6$  have been vibrationally analyzed in three electronic-vibrational transitions, it is now possible to propose reasonable assignments for the vibrational frequencies in the excited electronic states. In an electronic transition which is allowed by symmetry, only the totally symmetric frequencies are expected to appear in single quantum additions in the vibrational fine structure.<sup>14</sup> Except for the  $35\text{ cm.}^{-1}$  interval, all of the prominent intervals in the absorption spectra can be assigned to fundamental frequencies of the  $a_g$  class in the excited states, or to combinations of  $a_g$  fundamentals.

The correlation of the vibrational frequencies in various electronic states is given in Table IV. The frequencies marked  $\sim$  are estimated from the corresponding motions of the  $b_u$  class in the  ${}^1A_g$  ground electronic state. The  $2971\text{ cm.}^{-1}$  interval in the  ${}^1A_u \leftarrow {}^1A_g$  absorption transition of  $\text{Ac}_2$  is quite prominent, and is assigned to an  $a_g$   $\text{CH}_3$  stretching frequency in the  ${}^1A_u$  electronic state. The corresponding interval in  $\text{Ac}_2-d_6$  is expected to be approximately  $2100\text{ cm.}^{-1}$  and there are absorption lines in the appropriate region in the  $\text{Ac}_2-d_6$  crystal absorption spectrum, although this fundamental may be obscured by several combinations. The appearance of the  $\text{CH}_3$  stretching frequency in this  $n\text{-}\pi^*$  transition indicates that the electrons on the methyl groups are actually involved in the transition, and is evidence for some type of electronic interaction such as hyperconjugation of the  $\text{CH}_3$  groups with the  $\text{O}=\text{C}-\text{C}=\text{O}$  system.

The change in frequency of the  $a_g$  C=O stretching fundamental,  $\nu_1$ , and the  $a_g$  C-C stretching fundamental,  $\nu_2$ , in the excited electronic states is due to a change in the electronic distributions in these bonds in the excited states. In the  $n\text{-}\pi^*$  transitions, the electron is excited from a non-bonding orbital localized essentially on an O atom to a butadiene-like  $\pi^*$  antibonding orbital which extends over the  $\text{O}=\text{C}-\text{C}=\text{O}$  skeleton. A qualitative picture of the  $n$  and  $\pi\text{-LCAO-MO}$ 's for biacetyl is shown in Paper I, Fig. 6. The one-electron orbital jump  $n\text{-}\pi_3$  gives rise to configuration I, which differs from the ground  $\pi$ -electronic configuration in that there is an additional node in the C=O bonds

(14) H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).

and an additional antinode in the C-C bond. The one-electron orbital jump  $n-\pi_4$  gives rise to configuration II, which possesses additional nodes between the C=O and C-C bonds. Consequently,  $\nu_1$  is expected to decrease in states arising from both I and II whereas  $\nu_2$  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  $\pi$ -electronic distribution in the excited states. An examination of Table IV shows that these predictions are not borne out in detail. The value of  $\nu_1$  does decrease in I<sup>1</sup>A<sub>u</sub> and II<sup>1</sup>A<sub>u</sub>, but the increase of  $\nu_1$  in I<sup>3</sup>A<sub>u</sub> is quite unexpected, and is difficult to explain on the basis of a simple orbital picture. Moreover,  $\nu_2$  does not increase in either I<sup>3</sup>A<sub>u</sub> or I<sup>1</sup>A<sub>u</sub>, and the observed decrease of  $\nu_2$  is contrary to the simple predictions. The naive LCAO-MO configurational description which neglects electronic repulsion and changes in the  $\sigma$ -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*<sub>6</sub> 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.

BERKELEY 4, CALIFORNIA

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

## Some Divalent Metal Ethylenediammonium Phosphates; A New Series of Double Salts<sup>1</sup>

BY ROY C. MAST<sup>2</sup> AND RALPH E. OESPER

RECEIVED MAY 26, 1955

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<sub>2</sub>)(HPO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mg(enH<sub>2</sub>)(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·4.5H<sub>2</sub>O, Zn<sub>3</sub>(enH<sub>2</sub>)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>·5H<sub>2</sub>O, Zn<sub>2</sub>(enH<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub>, Zn(enH<sub>2</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>, Mn<sub>2</sub>(enH<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O, Mn<sub>2</sub>(enH<sub>2</sub>)(HPO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O, Mn(enH<sub>2</sub>)(P<sub>2</sub>O<sub>7</sub>)·H<sub>2</sub>O, Ni(enH<sub>2</sub>)(HPO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(enH<sub>2</sub>)(P<sub>2</sub>O<sub>7</sub>)·4H<sub>2</sub>O and Na<sub>2</sub>(enH<sub>2</sub>)(P<sub>4</sub>O<sub>10</sub>)·2H<sub>2</sub>O. 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.<sup>7</sup> 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.<sup>3</sup> Bassett, *et al.*,<sup>4</sup> 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,<sup>5</sup> the preparation of a series of ortho- and pyrophosphates of aliphatic diamines were described. In all of the products ob-

tained 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 pH 4.3 (pH meter) with sodium hydroxide solution.

Commercial crystalline pyrophosphoric acid<sup>6</sup> 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 pH 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 pH, *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

(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. Basse, G. 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, Ammonia, Alabama.