

## Metal Complexes of Ethyl Dimethylamidopyrophosphates

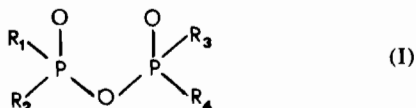
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Metal ion complexes of asym-diethyltetramethyldiamido-pyrophosphate (ASYM) and ethyl hexamethyltriamidopyrophosphate (MONE) have been prepared. Complexes of tetraethyl pyrophosphate (TEPP) are very difficult to isolate. Thus far, only an adduct of TEPP with antimony pentachloride has been isolated. The coordinating ability of ASYM, MONE, and TEPP is compared with that of octamethylpyrophosphoramidate (OMPA) and sym-diethyl tetramethyldiamidopyrophosphate (SYM). The order of coordinating ability is OMPA > MONE > SYM > ASYM > TEPP.

## Introduction

We have been examining the influence of organic substituents on the coordinating ability of the pyrophosphate linkage. In previous publications we have described complexes of ligands of general structural formula(I) where  $R_1 = R_2 = R_3 = R_4 = N(CH_3)_2$ ,



octamethylpyrophosphoramidate (OMPA);<sup>3</sup>  $R_1 = R_3 = OC_2H_5$  and  $R_2 = R_4 = N(CH_3)_2$ , sym-diethyl tetramethyldiamidopyrophosphate (SYM).<sup>4</sup> Previous work<sup>5,6</sup> has also indicated that the bridging atom can be changed from —O— to —N(CH<sub>3</sub>)— to —CH<sub>2</sub>— without affecting the coordinating ability of the phosphoryl sites.

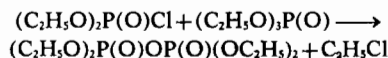
The present report describes the complexing ability of several other ligands of type I. These include  $R_1 = OC_2H_5$  and  $R_2 = R_3 = R_4 = N(CH_3)_2$  ethyl hexamethyltriamidopyrophosphate (MONE);  $R_1 = R_2 = OC_2H_5$  and  $R_3 = R_4 = N(CH_3)_2$ , asym-diethyltetramethyldiamidopyrophosphate (ASYM); and  $R_1 = R_2 = R_3 = R_4 = OC_2H_5$ , tetraethylpyrophosphate (TEPP).

## Experimental Section

*Toxicity.* All of the ligands described here are

highly toxic. Precautions were taken to avoid skin contact. Any excess ligand or metal complexes were hydrolyzed with sodium hydroxide solution before pouring down the drain. Organic pyrophosphates are anticholinesterase agents. The LD<sub>50</sub> values toward rats are 8.0, 11.5, 2.7, and 0.9 for OMPA, SYM, ASYM, and TEPP.<sup>7,8</sup> Atropine sulfate is a specific antidote.

*Preparation of Ligands.* (1) *Tetraethyl pyrophosphate (TEPP).* TEPP was prepared by two different methods. The first was the Schrader method<sup>9</sup> in which equimolar amounts of diethyl phosphorochloridate (Aldrich) (75 g) and triethyl phosphate (Aldrich) (79 g) are refluxed in 250 ml of *m*-xylene at 140°:



The use of solvent is optional. The ethyl chloride formed in the course of the condensation was collected using a cold finger filled with isopropanol—CO<sub>2</sub> slush. When no more ethyl chloride was evolved, the heating was stopped and the solvent stripped off with a rotoevaporator connected to a water aspirator. TEPP was vacuum distilled from the residue [bp 132° (1.3 mm)]. A 35% yield resulted. The distillate was found to be 82% pure.

The second synthetic method used to prepare TEPP was that of Toy.<sup>10</sup> A mixture of 7.14 g (0.396 mol or 2.2% excess) of water and 62.7 g (0.794 mol or 2.5% excess) of pyridine was slowly added with stirring from a dropping funnel to 133.7 g (0.775 mol) of diethyl phosphorochloridate. The temperature was maintained at 0°–2° by means of an ice bath. Upon completion of the addition (1 hr), the reaction mixture was stirred in the ice bath for 20 min and then heated slowly to 35° for 20 min. The mixture was then cooled and filtered. The pyridine hydrochloride was washed twice with anhydrous ether. The ether was stripped off the combined filtrate and ether washings, and the residue was subjected to vacuum distillation. TEPP was collected in 58% yield and analyzed to be 77.4% pure. A general statement which can be made regarding the relative merits of these two methods is that the hydrolytic method char-

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(3) M. D. Joesten, M. S. Hussain, P. G. Lenhart, *Inorg. Chem.*, **9**, 151 (1970), and references cited therein.  
(4) M. F. Prysak and M. D. Joesten, *Inorg. Chem.*, **8**, 1445 (1969).  
(5) K. P. Lannert and M. D. Joesten, *Inorg. Chem.*, **7**, 2048 (1968).  
(6) K. P. Lannert and M. D. Joesten, *Inorg. Chem.*, **8**, 1775 (1969).

(7) J. E. Gardiner and B. A. Kilby, *Biochem. J.*, **51**, 78 (1952).  
(8) K. P. DuBois and J. M. Coon, *Arch. Ind. Hyg. Occupational Med.*, **6**, 9 (1952).  
(9) G. Schrader, « Die Entwicklung neuer insektizider Phosphorsäure-Ester », 3rd. ed., Weinheim: Verlag Chemie, 1963, p. 358.  
(10) A. D. F. Toy, *J. Am. Chem. Soc.*, **70**, 3882 (1948).

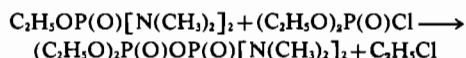
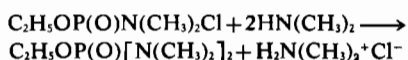
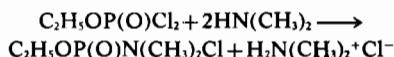
acteristically results in much higher yields than the Schrader method but unfortunately is not applicable to unsymmetrical pyrophosphate syntheses.

The Toy and Schrader products were combined (88 g) and dissolved in 400 ml of aqueous 9% sodium chloride and left standing for 5 min in a separatory funnel. The purpose of this operation is to selectively hydrolyze any higher polyphosphates present while ensuring that TEPP undergoes only minimal hydrolysis. After this time, the solution was shaken for 30 sec with benzene and the aqueous (lower) layer drawn off into another separatory funnel. The benzene was washed with 50 ml of 9% sodium chloride solution and the lower layer again drawn off into the same separatory funnel as before. The combined aqueous layers were shaken with 200 ml of benzene and the lower layer discarded. The two benzene layers were combined and shaken with 100 ml of ice water with the lower layer discarded again. The remaining benzene layer was stripped of solvent on the rotoevaporator and subjected to vacuum distillation. The TEPP distillate (55 g) was analyzed to be 100.0% pure.

The nmr spectrum of the distillate showed the correct relative areas for the methyl and methylenic proton resonances:  $\delta_{\text{neat}}$  1.33 (triplet, CH<sub>3</sub>, 12 H, area 130), 4.20 ppm (two overlapping quartets, CH<sub>2</sub>, 8 H, area 84). GLC showed a single peak (141 sec) in the pyrophosphate retention time region in the chromatogram of the distillate. Its ir spectrum conformed exactly to the literature ir.<sup>11</sup> Mass spectral analysis yielded a single peak in the mass unit region above 250. The peak corresponded to a molecular weight of slightly greater than 290. The calculated molecular weight for C<sub>8</sub>H<sub>20</sub>P<sub>2</sub>O<sub>7</sub> is 290.18. The analytical method used in determining TEPP purity was that of Dvornikoff and Morrill.<sup>12</sup>

(2) *sym-Diethyl tetramethyldiamidopyrophosphate (SYM)*. SYM was prepared according to the procedure of Holmstedt.<sup>13</sup> The details of this synthesis have been published.<sup>4</sup>

(3) *asym-Diethyl Tetramethyldiamidopyrophosphate (ASYM)*. ASYM was prepared using a modified Schrader method as found in a British patent.<sup>14</sup> The following reactions were employed:



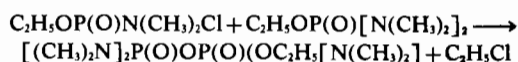
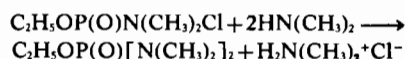
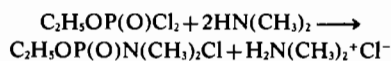
Ethyl dimethylphosphoramidochloridate was prepared as in the SYM synthesis only, rather than isolating the pure compound by vacuum distillation after stripping off the ether, the residue was returned to the 2 l

flask and redissolved in 1 l of anhydrous ether. After cooling to below 5°, 2 moles of dimethylamine in 500 ml of anhydrous ether were slowly added as before. After filtering and stripping, the filtrate was subjected to vacuum distillation and ethyl tetramethylphosphorodiamidate [bp 59° (1 mm)] isolated in 70% yield.

ASYM was prepared in the following manner. Ethyl tetramethylphosphorodiamidate (100 g, 0.56 mol) was stirred with diethyl phosphorochloridate (Aldrich) (96.6 g, 0.56 mol) at 85° until no further ethyl chloride condensed on the cold finger containing isopropanol-CO<sub>2</sub> slush. Use of a solvent is optional. We found the reaction worked just as well without solvent as it did in benzene. The time of heating was approximately 2 hrs. The condensation was carried out under a weak nitrogen flow so as to aid ethyl chloride evolution. ASYM [bp 140° (1.5 mm)] was vacuum distilled from this reaction mixture using a 50 ml pot and collecting the distillate in fractions. A 30% yield resulted.

The nmr of the distillate indicated purity not only because the integrated peak areas appeared in the correct ratio, but also because only a single doublet appeared for the dimethylamino proton resonance:  $\delta_{\text{neat}}$  1.31 (triplet, CH<sub>3</sub>, 6 H, area 76), 2.67 (doublet, N-CH<sub>3</sub>, 12 H, area 160), 4.17 ppm (two overlapping quartets, CH<sub>2</sub>, 4H, 54). The ir spectrum of the distillate was the same as the literature ir spectrum.<sup>15</sup> GLC showed only one peak (194 sec) in the pyrophosphate retention time region in the chromatogram of the distillate. Mass spectral analysis indicated a compound of molecular weight slightly greater than 288. The calculated molecular weight for C<sub>8</sub>H<sub>22</sub>N<sub>2</sub>P<sub>2</sub>O<sub>5</sub> is 288.23. Elemental analyses further confirmed the purity of ASYM as shown in Table I.

(4) *Ethyl hexamethyltri amidopyrophosphate (MONE)*. MONE was prepared using a modified Schrader method illustrated by the following equations:



The preparations of ethyl dimethylphosphoramidochloridate and ethyl tetramethylphosphorodiamidate were described previously in the SYM<sup>4</sup> and ASYM syntheses respectively.

Ethyl tetramethylphosphorodiamidate (100 g, 0.56 mol) and ethyl dimethylphosphoramidochloridate (96.1 g, 0.56 mol) were stirred at 85° under nitrogen until no further ethyl chloride was evolved. No solvent was used. The time of complete ethyl chloride evolution was approximately 6 hrs. MONE [bp 138° (2 mm)] was then collected in fractions from the vacuum distillation of the resulting solution using a 50 ml distilling pot. A 30% yield resulted.

The nmr of the distillate exhibited peak areas in the correct ratio:  $\delta_{\text{neat}}$  1.30 (triplet, CH<sub>3</sub>, 3 H, area 28, 2.65 (two doublets, N-CH<sub>3</sub>, 6 H and 12 H, area

(11) B. Holmstedt and L. Larsson, *Acta Chem. Scand.*, 5, 1179 (1951).

(12) M. Dvornikoff and H. Morrill, *Anal. Chem.*, 20, 935 (1948).

(13) B. Holmstedt, *Acta. Physiol. Scand.*, 25, suppl. 90 (1951).

(14) Monsanto Chemical Co., Brit. Patent 732, 384 (1955); *Chem. Abstr.*, 50, 7122 i (1956).

Table I. Analytical Results

Compound	% Carbon		% Hydrogen		% Nitrogen	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
Mg(MONE) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	26.5	26.3	6.4	6.3	11.6	12.0
Co(MONE) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	25.7	25.5	6.2	6.2	11.3	11.7
Ni(MONE) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	25.7	25.2	6.2	6.1	11.3	11.2
Cu(MONE) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	23.0	23.2	5.5	5.6	10.0	10.4
Li(MONE)ClO <sub>4</sub>	24.4	25.3	5.9	6.4	10.7	11.7
HfCl <sub>4</sub> · MONE	15.8	14.9	3.8	4.1	6.9	7.5
2TiF <sub>4</sub> · MONE	18.0	17.3	4.3	4.6	7.9	8.9
ASYM	33.3	33.5	7.7	7.8	9.7	9.5
Co(ASYM) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	25.7	23.4	5.9	5.8	7.5	7.9
Cu(ASYM) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	22.9	22.2	5.3	5.4	6.7	7.4
2SbCl <sub>5</sub> · ASYM	10.8	8.2	2.5	2.4	3.2	3.5
Sr(ASYM) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	22.3	22.2	5.1	5.0	6.5	7.8
2SbCl <sub>5</sub> · TEPP	10.8	11.0	2.3	2.4		

167), 4.05 ppm (two overlapping quartets, CH<sub>2</sub>, 2 H, area 19). More important as an indicator of the purity of MONE was the fact that the dimethylamino resonance consisted of two doublets in a ratio of 2:1. The ir spectrum of the distillate agreed with the literature ir spectrum.<sup>15</sup> GLC showed only one peak (219 sec) in the pyrophosphate retention time region of the chromatogram indicating only a single pyrophosphate in the distillate. Mass spectral analysis showed a single strong peak at slightly greater than 287 mass units. The calculated molecular weight for C<sub>8</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>P<sub>2</sub> is 287.23.

**Preparation of Complexes.** (1) *General Methods.* Four general methods were used in the syntheses of metal complexes. The most commonly used method utilizes 2,2-dimethoxypropane (DMP) as a dehydrating agent,<sup>16</sup> referred to hereafter as the DMP method. A typical preparation by the DMP method involved dissolving 0.3 g ( $8.2 \times 10^{-4}$  mol) of hydrated nickel perchlorate in 3 ml of DMP, adding 1.0 g ( $3.5 \times 10^{-3}$  mol) of ligand (mol wt = 288), and stirring for 15 min. Excess anhydrous ether was then added. If an oil formed, it was repeatedly extracted with ether until it solidified.

The second method employed was the EOF method which uses ethyl orthoformate (EOF) as the dehydrating agent.<sup>17</sup> The use of EOF allows syntheses which could not be accomplished with DMP. EOF acts faster and more completely in polar media than DMP does.

A typical preparation by the EOF method involved dissolving 0.3 g ( $8.2 \times 10^{-4}$  mol) of hydrated nickel perchlorate in 5 ml of ethanol and adding 1.5 g ( $5.2 \times 10^{-3}$  mol) of ligand (mol wt = 290) and 1.1 g ( $7.4 \times 10^{-3}$  mol) of EOF (Matheson). After stirring the solution for 30 min, excess ether was added to precipitate out the complex as either a solid or oil. If the result was an oil, the repetitive ether extraction techniques described in the DMP method were used to work up the oil.

A third method used the ligand as the solvent (LS method). The LS method involved dissolving the metal perchlorate in a large excess of ligand and precipitating the solid or oil with anhydrous ether. The

ether extraction techniques with oils as outlined in the DMP method were used to work up the oils. The LS method applied to Lewis acid adduct synthesis was similar. The only difference was that excess benzene was used to precipitate the adduct from the Lewis acid-pyrophosphate solution.

The LS method appeared to be the best of the complex preparation methods not only because it kept possible interfering effects to a minimum but also because it was applicable to all types of complex preparations. Thus the LS method can be substituted for any of the other methods.

A fourth method utilized was the THF method. This method was used exclusively in the Lewis acid adduct preparations but may also work in place of the more conventional preparative procedures such as the DMP method. The THF method utilized tetrahydrofuran (THF) as the solvent and was patterned after the work of Muetterties.<sup>18</sup> A typical adduct preparation by the THF method involved saturating THF with a Lewis acid, and adding the ligand. Excess carbon tetrachloride was then added to aid in precipitating the adduct. Upon standing for periods of up to one day (depending on the ligand) the adduct precipitated. If no solid appeared after this time, the LS method was tried.

When a solid was obtained by any of the above methods, it was filtered and washed with the appropriate solvent. The compound was dried *in vacuo*.

(2) *Complexes of TEPP.* The only TEPP compound isolated in the solid state was an antimony pentachloride adduct. It was prepared by dissolving 3.0 g ( $1.0 \times 10^{-2}$  mol) of SbCl<sub>5</sub> in 40 ml of carbon tetrachloride and adding 0.8 g ( $2.8 \times 10^{-3}$  mol) of TEPP. The white adduct precipitated immediately. All other Lewis acids which were tried (TiF<sub>4</sub>, ZrF<sub>4</sub>, ZrCl<sub>4</sub>, HfCl<sub>4</sub>) failed to give any isolable adducts by either the THF or LS methods.

Only oils were obtained when DMP, EOF, and LS methods were used for reactions of all types of metal perchlorate salts with TEPP.

(3) *Complexes of ASYM.* The LS method yielded solids with cobalt(II) and copper(II) perchlorates. The anhydrous ether used was dried over calcium hydride. The attempted preparations of an antimony

(15) R. Harvey and J. Mayhood, *Can. J. Chem.*, **33**, 1552 (1955).

(16) K. Starke, *J. Inorg. Nucl. Chem.*, **11**, 77 (1959).

(17) P. van Leeuwen and W. Groeneveld, *Inorg. Nucl. Chem. Letters*, **3**, 145 (1967).

(18) E. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

pentachloride adduct resulted in a gummy white solid which could not be successfully dried *in vacuo*.

(4) *Complexes of MONE*. Metal perchlorate complexes of MONE were prepared by both DMP and LS methods. A MONE adduct of  $TiF_4$  was prepared by the LS method with intermittent heating to aid dissolution. Excess benzene was added to complete precipitation of the adduct. Hafnium tetrachloride was reacted with MONE according to the THF method.

*Conductance Measurements*. A conductance bridge manufactured by Industrial Instruments and equipped with a platinum dip-type cell (cell constant  $0.110\text{ cm}^{-1}$ ) was used to measure the conductance of nitromethane solutions of the complexes.

*Spectral Measurements*. The infrared spectra of the complexes were obtained with a Beckman IR-10 either as Nujol mulls between sodium chloride plates or as KBr pellets.

Visible and near-infrared solution spectra were obtained with a Beckman DK-2A spectrophotometer by using matched 1 cm quartz cells. Acetone was the solvent for most electronic spectra measurements.

The visible and near-infrared solid reflectance spectra were obtained using a Cary Model 14 Recording Spectrophotometer fitted with a Cary Cell-Space Total Diffuse Reflectance Accessory. The reference was a freshly cut surface of a magnesium carbonate block.

All nmr spectra were obtained at ambient temperature with a Varian A-60 NMR spectrometer. Ligand spectra were obtained neat. Deuteriochloroform was used as the solvent for spectra of metal complexes. Tetramethylsilane (TMS) was used as the internal standard in all spectra.

The mass spectra of the ligands were run by Mr. C. T. Wetter of Vanderbilt University on an LKB 9000 Gas Chromatograph-Mass Spectrometer.

*Magnetic Susceptibility Measurements*. All measurements were made at room temperature by using the Faraday method with mercury(II) tetrathiocyanatocobaltate(II) as the reference. Diamagnetic corrections were determined by measuring the magnetic susceptibility of the corresponding zinc(II) complex.

*Gas Chromatographic Analysis*. All GLC analyses were performed on a F and M Model 720 Dual Column Programmed Temperature Chromatograph with a thermal conductivity detector. The instrument settings were oven temperature,  $200^\circ$ ; injection port temperature,  $260^\circ$ ; detector temperature,  $260^\circ$ ; bridge current, 100 ma; helium pressure, 22.5 psi; attenuation, 8; flow rate, 60 cc/min; chart speed, 120 in/hr. Retention times for the organic pyrophosphates on a 6 ft, 10% Sil Gum Rub, SE-30, 80-100 S, 7204 column were as follows: TEPP-141 sec, SYM-166 sec, ASYM-194 sec, MONE-219 sec, OMPA-269 sec.

## Results and Discussion

Table I lists the compounds which were isolated as solids in this study. Complexes of MONE first separated as oils similar to the complexes of SYM

reported earlier.<sup>4</sup> Solid complexes of ASYM with  $Co^{II}$  and  $Cu^{II}$  were obtained only after repeated extractions with ether. Only intractable oils were obtained from TEPP reactions with metal perchlorates. All the complexes in Table I are hygroscopic. The relative ease of isolation of complexes of organopyrophosphates is  $OMPA > MONE > SYM > ASYM > TEPP$ . This is the order one would expect on the basis of the greater releasing ability of the dimethylamino group. Stability constant measurements for OMPA and SYM with  $Ni^{II}$  and  $Co^{II}$  also support the above order.<sup>4</sup> However, this is *not* the order indicated by ligand field parameters.

*Conductance Measurements*. All of the complexes of perchlorate salts have molar conductance values which fall in the expected ranges for 1:1 or 2:1 electrolytes. These will not be tabulated since no evidence of coordinated perchlorate was found. The molar conductance of  $10^{-3} M$   $2SbCl_5 \cdot TEPP$  is 108 at  $25^\circ C$ . This is a little higher than the 80-90 range generally found for 1:1 electrolytes in nitromethane. A possible structure for the adduct is  $[SbCl_4 \cdot TEPP] \cdot [SbCl_6]$ . The conductance data indicate that some additional chloride ion is dissociating in solution.

*Magnetic Moments*. The magnetic moments at room temperature are those expected for spin-free complexes.

*Nuclear Magnetic Resonance Studies*. Figures 1 and 2 are representative nmr spectra for SYM and MONE. The pyrophosphates studied showed three general resonance areas: (1) the methyl protons of the ethoxy group split by the methylenic protons of the ethoxy group and the phosphorus to which the ethoxy group is bonded. (2) the methylenic protons

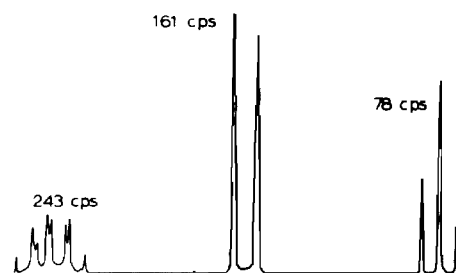


Figure 1. The proton nmr spectrum of SYM(neat) with resonance centers as indicated. Reference is tetramethylsilane.

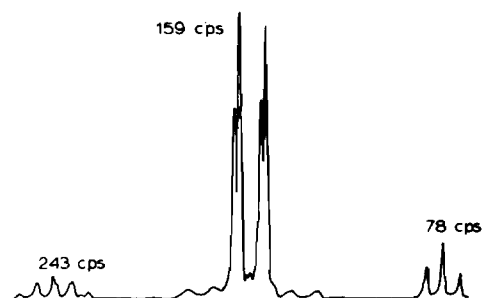


Figure 2. The proton nmr spectrum of MONE(neat) with resonance centers as indicated. Reference is tetramethylsilane.

Table II. Protonic Resonance Centers <sup>a</sup>

Compound	Solvent	CH <sub>2</sub> (EtO)	CH <sub>3</sub> (EtO)	CH <sub>3</sub> (NMe <sub>2</sub> )
OMPA	neat			160
OMPA	CDCl <sub>3</sub>			163
Zn(OMPA) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	CDCl <sub>3</sub>			165
MONE	neat	243	78	159
MONE	CDCl <sub>3</sub>	253	83	166
Mg(MONE) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	CDCl <sub>3</sub>	251	84	167
SYM	neat	243	78	161
SYM	CDCl <sub>3</sub>	246	82	164
Zn(SYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	CDCl <sub>3</sub>	254	84	169
ASYM	neat	250	79	160
ASYM	CDCl <sub>3</sub>	253	82	162
Mg(ASYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub> <sup>b</sup>	CDCl <sub>3</sub>	260	85	166
TEPP	neat	252	80	
TEPP	CDCl <sub>3</sub>	254	81	

<sup>a</sup> Spectra obtained at ambient temperature. <sup>b</sup> Dissolved in CDCl<sub>3</sub> as an oil.

of the ethoxy group split by the adjacent methyl protons and the phosphorus to which the ethoxy group is bonded. (3) the dimethylamino protons split by the phosphorus to which they are bonded. Additional peaks are formed when non-equivalence exists among the ethoxy or dimethylamino groups (see Figure 2). The nmr data are presented in the form of resonance centers in Table II. A resonance center is simply the median frequency of a particular protonic resonance. For example, the nmr spectrum of OMPA has a simple doublet at 157 and 168 cps with TMS as the reference so the dimethylamino proton resonance center is at 163 cps. All resonance centers are in cycles per second with respect to TMS. The group on which the protons are located is identified in parentheses next to the proton types. Resonance centers of several diamagnetic complexes are also included in the data.

It has been reported previously that the OMPA doublet is shifted downfield in Zn(OMPA)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> in methylene chloride.<sup>19</sup> We also found such a shift in deuteriochloroform although not as great as reported. Resonance centers of MONE showed little, if any change upon coordination. However, both SYM and ASYM resonance centers showed small downfield shifts upon coordination as indicated in Table II.

The coupling constants deduced from the ligand spectra are unchanged in the diamagnetic metal ion complex spectra in the case of ASYM, SYM, and OMPA. In the spectrum of Mg(MONE)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>, J<sub>αH-βH</sub>, J<sub>αH-P</sub>, J<sub>βH-αH</sub>, J<sub>βH-P</sub>, and J<sub>H<sub>CNP</sub></sub> are unchanged from the MONE spectrum. However, the long range coupling constant J<sub>H<sub>CNP</sub>OP</sub> is changed. In five MONE spectra, that is, ten J<sub>H<sub>CNP</sub>OP</sub> values, the J<sub>H<sub>CNP</sub>OP</sub> range found was 1.6-2.3 cps. In three Mg(MONE)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> spectra, that is, six J<sub>H<sub>CNP</sub>OP</sub> values, the J<sub>H<sub>CNP</sub>OP</sub> range was 3.8-4.4 cps. Thus, J<sub>H<sub>CNP</sub>OP</sub> appears to have doubled in the complex. The uniqueness of J<sub>H<sub>CNP</sub>OP</sub> should be obvious. All other coupling constants are for short-range coupling; the coupling is only incidentally involved with the chelate ring formed upon complexation and hence, the coupling constant remains unchanged in the coordination act. However, because of the nonequivalence of the phosphorus nuclei in MONE, J<sub>H<sub>CNP</sub>OP</sub> must be postulated, and it should be

intimately involved with and highly sensitive to any electron density shifts brought about in the coordination act. Since the coupling constant has doubled in Mg(MONE)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>, it is obvious that coupling has been facilitated by the formation of a chelate ring. This effect may be due to some electron delocalization in the chelate ring which would facilitate the long-range coupling process.

*Infrared Band Assignments.* The P=O and P-O-(P) stretching frequencies are listed in Table III for the free ligands.

Table III. Infrared Band Assignments

	P=O	P-O-(P)
TEPP	1300 cm <sup>-1</sup>	948 cm <sup>-1</sup>
SYM	1260	930
ASYM	1254, 1296	943
MONE	1240, 1270	928
OMPA	1230	928

Other frequency assignments are possible. The C-O-(P) vibration is found at 1173 cm<sup>-1</sup> in TEPP, SYM, and ASYM but is too weak to be observed in MONE. The P-O-(C) vibration occurs at 1035 cm<sup>-1</sup> in TEPP, SYM, and ASYM but occurs only as a shoulder in MONE at 1030 cm<sup>-1</sup>. The C-C stretch is obvious only in TEPP at 980 cm<sup>-1</sup>. Bands from the P-NMe<sub>2</sub> structure are characteristic of the 1300, 1180, 1065, and 975 cm<sup>-1</sup> regions. Thus, SYM possesses P-NMe<sub>2</sub> peaks at 1320, 1197, and 1055 cm<sup>-1</sup> with the 975 cm<sup>-1</sup> peak obscured by the P-O-(C) and P-O-(P) bands. The ligand ASYM possesses P-NMe<sub>2</sub> peaks at 1316, 1194, and 994 cm<sup>-1</sup> with the 1065 cm<sup>-1</sup> frequency swamped out by the P-O-(C) band. The ligand MONE exhibit P-NMe<sub>2</sub> peaks at 1315, 1193, 1059, and 995 cm<sup>-1</sup>. The ligand OMPA shows P-NMe<sub>2</sub> bands at 1310, 1073, and 998 cm<sup>-1</sup> with the P=O peak reducing the 1180 cm<sup>-1</sup> band to a shoulder. Band assignments were made using the data of Thomas and Chittenden.<sup>20</sup>

Coordination to the phosphoryl oxygen atoms is in-

(19) M. D. Joesten and R. A. Jacob, in «The Chemistry of Lanthanide and Actinide Elements», Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1967, p. 13.

(20) R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, **22**, 1449 (1966).

**Table IV.** Visible and Near-Infrared Data of Isolated Complexes

Compound	Acetone Solution		$\lambda_{\max}$ , $m\mu$ ( $cm^{-1}$ )
	$\lambda_{\max}$ , $m\mu$ ( $cm^{-1}$ )	$\epsilon$	
Co(ASYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub> <sup>a</sup>	544(18382)	24	542(18450)
Co(ASYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	541(18484)	23	
Cu(ASYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	912(10964)	62	877(11402)
Co(SYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	540(18518)	17	541(18484)
Ni(SYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	424(23584)	15	425(23529)
	680 sh(14705) <sup>d</sup>	3	685 sh(14598)
	800(12500)	6	794(12594)
	1358(7364)	5	1380(7246)
Ni(SYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub> <sup>b</sup>	425(23529)	15	
	682 sh(14662)	3	
	807(12391)	6	
	1382(7236)	5	
Cu(SYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	945(10582)	17	890(11235)
Co(MONE) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	543(18416)	23	543(18416)
Ni(MONE) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	425(23529)	18	426(23474)
	680 sh(14705)	2	684 sh(14619)
	808(12376)	5	799(12515)
	1383(7231)	4	1365(7326)
Cu(MONE) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	913(10592)	29	927(10787)
Cu(MONE) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> <sup>c</sup>	958(10483)		

<sup>a</sup> In nitromethane. <sup>b</sup> In SYM. <sup>c</sup> 10 drops of MONE added to 3 ml of solution. <sup>d</sup> sh indicates shoulder here and in succeeding tables.

**Table V.** Visible and Near-Infrared Data Using Ligand as Solvent

Species	Solvent	$\lambda_{\max}$ , $m\mu$ ( $cm^{-1}$ )
Co(TEPP) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	TEPP	536(18656)
Co(ASYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	ASYM	542(18450)
Co(SYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	SYM	541(18484)
Ni(TEPP) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	TEPP	413(24213), 674 sh(14836)
		774(12919)
Ni(ASYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	ASYM	424(23584), 682 sh(14662)
		819(12210)
Ni(SYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	SYM	424(23584), 630 sh(15873)
		749(13351)
Cu(TEPP) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	TEPP	935(10695)
Cu(ASYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	ASYM	942(10615)
Cu(SYM) <sub>3</sub> (ClO <sub>4</sub> ) <sub>2</sub>	SYM	930(10752)

**Table VI.** Ligand Field Parameters toward Nickel(II)

Ligand	Phase	Dq	$\beta^\circ$
TEPP	acetone	800 $cm^{-1}$	0.11
TEPP	TEPP	768	0.11
ASYM	acetone	746	0.12
ASYM	ASYM	717	0.10
SYM	acetone	741	0.12
SYM	SYM	806	0.20
SYM	solid	746	0.13
MONE	acetone	735	0.12
MONE	solid	740	0.13
OMPA	acetone	726	0.11
OMPA	solid	750	0.14

indicated by the observed decrease in the P—O stretching frequency. Changes ranged from 20 to 50  $cm^{-1}$  depending on the metal ion and the ligand.

**Electronic Spectral Data.** Electronic absorption spectral data are listed in Table IV. Compounds listed in Table IV were previously isolated as solids and analyzed before definite amounts were dissolved in acetone. The reflectance spectral data for the solids are given in the last column. The spectra of the compounds listed in Table V were run by dissolving

the corresponding metal perchlorate in the ligand as the solvent. Any necessary dilution was carried out with more ligand. The reference cell was filled with the ligand for the measurements summarized in Table V. Ni(OMPA)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> and Ni(MONE)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> are not included because they are insoluble in OMPA and MONE, respectively. Since the spectrum of the nickel(II) complex of TEPP in Table V agrees with the spectra of all the other nickel(II) complexes with respect to the relative intensities of the <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> (P) and <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> (F) bands,<sup>21</sup> octahedral symmetry was assumed for the TEPP complex of nickel(II).

Octahedral nickel(II) spectra characteristically exhibit three bands in the visible and near ir region. The sharp blue band usually occurs in the 370-450  $m\mu$  region and corresponds to the <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> (P) transition. The moderately broad middle band (often with a shoulder) is found in the 600-900  $m\mu$  region and corresponds to the <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> (F) transition. The diffuse 10Dq band usually occurs in the 1000-1500  $m\mu$  region and corresponds to the <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub> transition.

We calculated Dq by two methods. The first involves selection of the Dq value from the 10 Dq band

(21) C. K. Jorgensen, *Acta Chem. Scand.*, 9, 1362 (1955).

in the near ir.<sup>22,23</sup> The middle band is then calculated by using this experimental  $Dq$  and the matrix elements given by Orgel;<sup>24</sup> this result is then compared with the experimental value of the middle band. Good agreement between the calculated and experimental middle

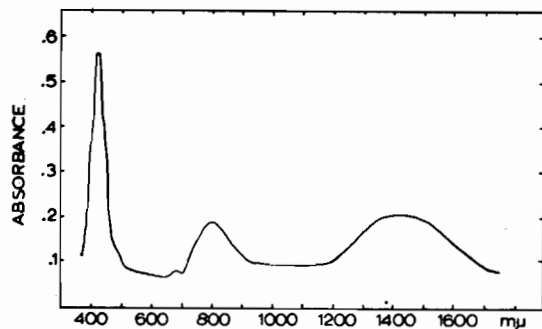


Figure 3. The visible and near-infrared spectrum of 0.04 M  $\text{Ni}(\text{SYM})_3(\text{ClO}_4)_2$  in acetone.

(22) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

(23) R. S. Drago, « Physical Methods in Inorganic Chemistry », Reinhold Publishing Corp., New York, N. Y., 1965, p. 410.

(24) L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

band values is reportedly indicative of octahedral symmetry in solution and accuracy in the selection of band maxima. The second method uses experimental values of the blue and middle bands in a quadratic equation to calculate the  $Dq$  value.<sup>25</sup>

The diffuse character of the 10  $Dq$  band makes selection of a band maximum difficult. This is illustrated in Figure 3 for  $\text{Ni}(\text{SYM})_3(\text{ClO}_4)_2$ . Therefore, we have used the second method to avoid the need for determining a 10  $Dq$  band maximum. Table VI lists the ligand field parameters for solid  $\text{Ni}^{II}$  complexes and solutions of  $\text{Ni}^{II}$  complexes in the ligand as solvent. The  $Dq$  results are ambiguous since values obtained from spectra of solids are essentially equal while values obtained in acetone solution are  $\text{TEPP} > \text{ASYM} > \text{SYM} > \text{MONE} > \text{OMPA}$ . We feel that ligand field parameters are not a reliable criterion for predicting coordinating ability of ligands, particularly in the case of ligands containing the phosphoryl donor site.

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(25) A. E. Underhill and D. E. Billing, *Nature*, **210**, 834 (1966).