slower. The present work focuses attention on the primary step.[13]

A number of changes in the Raman spectrum of the SbF_6^- species should be observed when the first hydrolysis step occurs to form $SbF_5(OH)^-$. New fundamentals should be evident, notably one associated with the Sb–O stretching mode. Because the study involves aqueous solutions, the O–H fundamentals of the $SbF_5(OH)^-$ species are expected to be masked by those of the solvent. New Sb–F stretching and deformation vibrations are also to be expected and are observed.

The Sb–O stretching fundamental occurs at 692 cm^{-1} (Figure 2, top) and decreases in intensity as the HF concentration is increased (Figure 2, middle and bottom). The frequency agrees with work on a series of antimonate salts by Siebert[14] and the intensity pattern, with respect to the lower frequency Sb–F stretching fundamentals, is similar to that observed by Burger for the structurally related neutral TeF_5OH species.[15]

The two Raman-active Sb–F stretching fundamentals in $NaSbF_6$ change to four in aqueous solution at 649, 638, 573, and 557 cm^{-1}. As HF is added and the hydrolysis is suppressed, the Raman lines at 638 and 557 cm^{-1} decrease substantially in intensity as expected. The low-frequency ν_5 deformation fundamental in $NaSbF_6$ has a substantially larger bandwidth in aqueous solution which supports the view that the overall band corresponds to more than one fundamental. Increased HF concentration narrows the line width as expected if hydrolysis were being suppressed (Figure 2 top to bottom).

In addition to the above observations, a very weak, broad Raman band was centered at 170 cm^{-1}. Although this may refer to fundamental(s) of the $SbF_5(OH)^-$ species, it is more likely to represent the well-known intermolecular 170-cm^{-1} band of the solvent. The presence of HF greatly reduces the intensity of this band.[3]

The evidence strongly indicates that $SbF_5(OH)^-$ is formed in aqueous solutions of $NaSbF_6$ and that HF reverses the hydrolysis. It is valid to note, however, that the 649-cm^{-1} line occurs both in aqueous and in strongly HF solutions. Thus on this basis it is difficult to say whether the aqueous solution contains $SbF_5(OH)^-$ ions alone or a mixture of $SbF_5(OH)^-$ and SbF_6^- ions. Because of structural similarities, accidental degeneracies would not be surprising. A comparison of relative intensities of the 649- and 278-cm^{-1} lines in Figure 2 (top and bottom), where the Sb concentration varies almost tenfold, suggests that in aqueous solution the SbF_6^- species, if present, is roughly lower in concentration by an order of magnitude from that of the $SbF_5(OH)^-$ species. Therefore, the ambiguity is narrowed to the case where $SbF_5(OH)^-$ only is present or where $SbF_5(OH)^-$ and a relatively small amount of SbF_6^- are present in aqueous solution.

Acknowledgment.—Chemical analyses of solutions for Na, Sb, and F as well as analytical studies dealing with the complete hydrolysis of $NaSbF_6$ were performed by Mr. L. D. Blitzer and are very greatly appreciated.

---

[13] Solutions containing $NaSbF_6$ in low concentrations in water and in moderately strong HF were found to yield Raman spectra definitely more complicated than those presented in Figure 2, when the solutions were examined about 2 weeks after preparation. The spectral complications involved the region above ~550 cm^{-1} primarily, but no attempt was made to identify the species responsible by means of contour analysis. Instead emphasis was placed on studies involving high concentrations.

[14] H. Siebert, *Z. Anorg. Allg. Chem.*, **301**, 161 (1959).

[15] H. Burger, *ibid.*, **360**, 97 (1968).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE 37203

Metal Complexes of *P,P'*-Dialkyl-*N,N,N',N'*-tetramethylpyrophosphoramide

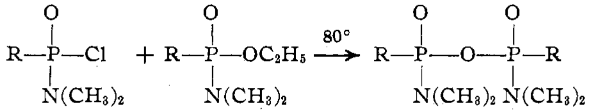
BY MELVIN D. JOESTEN* AND YING TAR CHEN

Received May 11, 1971

The present work is part of a continuing investigation of the influence of organic substituents on the coordinating ability of the pyrophosphate linkages.[1] Complexes of ligands with one alkyl group and one dimethylamino group attached to each phosphorus atom in a pyrophosphate linkage have been prepared and characterized. ^{31}P nmr spectroscopy has been used to detect the presence of asymmetric phosphorus atoms in the ligands.

Experimental Section

A. Preparation of Ligands.—*Caution! The organophosphorus compounds described below are toxic anticholinesterase agents and should be handled with care.* The general reaction used to prepare the ligands was



$$R-\underset{\underset{N(CH_3)_2}{|}}{\overset{\overset{O}{|}}{P}}-Cl + R-\underset{\underset{N(CH_3)_2}{|}}{\overset{\overset{O}{|}}{P}}-OC_2H_5 \xrightarrow{80°} R-\underset{\underset{N(CH_3)_2}{|}}{\overset{\overset{O}{|}}{P}}-O-\underset{\underset{N(CH_3)_2}{|}}{\overset{\overset{O}{|}}{P}}-R$$

1 2 3

where R is CH_3, C_2H_5, or i-C_3H_7.

Compound 1 was prepared from the corresponding alkylphosphonyl dichloride by literature methods.[2,3] Compound 2 was prepared from ethylalkylphosphonic chlorides[4-6] by the method of Crofts and Fox.[2]

Compound 3 was prepared by heating 1 with an equivalent amount of 2 under nitrogen at 80° for about 6 hr. The evolved ethyl chloride was collected in a trap cooled with a Dry Ice–acetone bath. The reaction mixture was distilled under vacuum. Fractions were collected at 135–140° (3 mm) for R = CH_3, 117–119° (0.3 mm) for R = C_2H_5, and 135–140° (2 mm) for R = i-C_3H_7. The yields were about 20% for all ligands.

B. Preparation of Complexes.—All complexes were prepared in 50–75% yield by the same method. Excess 2,2-dimethoxypropane was added to 1.366 mmol of the hydrated perchlorate dissolved in a minimum amount of acetone. This mixture was stirred for 45 min at room temperature. Then 5.5 mmol of ligand was added directly to the mixture. If the complex did not precipitate from solution at this point, excess ether was added, In some cases oils were obtained initially which were worked up with ether. All complexes are hygroscopic.

C. Physical Measurements.—Infrared spectra were obtained as KBr pellets with a Beckman IR-10 spectrophotometer. Visible and near-infrared spectra of nitromethane solutions of the complexes were recorded with a Cary 14 spectrophotometer.

---

[1] M. F. Prysak and M. D. Joesten, *Inorg. Chim. Acta*, **4**, 383 (1970), and references cited therein.

[2] P. C. Crofts and I. S. Fox, *J. Chem. Soc.*, 2995 (1958).

[3] P. C. Crofts and G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **75**, 3379 (1953).

[4] H. F. Moore and J. H. Williams, *J. Chem. Soc.*, 1465 (1947).

[5] A. J. Razumov, O. A. Mukhacheva, and E. A. Markovick, *Zh. Obshch. Khim.*, **27**, 2389 (1957); *Chem. Abstr.*, **52**, 7193*c*, (1958).

[6] M. F. Hersman and L. F. Audrieth, *J. Org. Chem.*, **23**, 1889 (1958).

TABLE I
DATA FOR COMPLEXES

Compound	Analytical data, %						Conductivity data Λ_{molar},[b] cm² ohm⁻¹ mol⁻¹	Magnetic moments[c] μ_{eff}, BM
	Carbon[a]		Hydrogen		Nitrogen			
	Calcd	Found	Calcd	Found	Calcd	Found		
$Co(M)_3(ClO_4)_2$	22.9	23.2	5.77	5.83	8.92	8.69	204	5.23
$Ni(M)_3(ClO_4)_2$	22.9	23.3	5.77	5.99	8.92	8.84	206	3.28
$Cu(M)_3(ClO_4)_2$	22.8	22.5	5.74	5.74	8.87	8.20	196	1.70
$Mg(M)_3(ClO_4)_2$	23.8	24.2	5.99	6.18	9.26	9.14	181	...
$Co(E)_3(ClO_4)_2$	28.1	27.7	6.48	6.65	8.19	8.18	204	5.58
$Ni(E)_3(ClO_4)_2$	28.1	27.4	6.48	6.80	8.19	8.40	198	3.51
$Cu(E)_3(ClO_4)_2$	27.9	27.1	6.45	6.07	8.15	7.99	180	1.50
$Mg(E)_3(ClO_4)_2$	28.8	28.3	6.64	6.54	8.39	8.53	188	...
$Co(P)_3(ClO_4)_2$	32.4	32.3	7.07	7.19	7.56	7.58	196	5.22
$Ni(P)_3(ClO_4)_2$	32.4	32.0	7.07	6.63	7.56	7.45	195	3.32
$Cu(P)_3(ClO_4)_2$	32.3	31.3	7.04	6.96	7.52	6.36	192	...
$Mg(P)_3(ClO_4)_2$	33.5	33.3	7.30	7.40	7.81	7.61	191	...

[a] Elemental analyses were done by Chemalytics, Tempe, Ariz. [b] Measurements were made for 10^{-3} *M* nitromethane solutions at 25°. [c] Measured at 297.5°K.

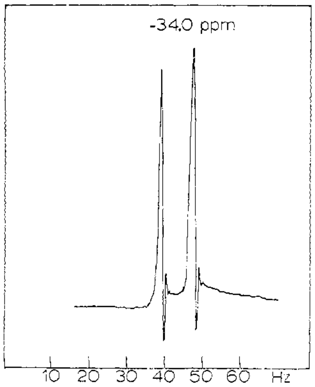


Figure 1.—Proton-decoupled ^{31}P nmr spectrum of a 50:50 mixture of I with benzylamine. Chemical shift is downfield from 85% H_3PO_4.

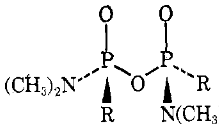
Proton nmr spectra were obtained at ambient temperature with a Varian A-60 nmr spectrometer. ^{31}P nmr spectra were obtained with a Varian XL-100-15 spectrometer operating at 40.5 MHz. The sample was contained in a 5-mm precision-bore nmr tube which was centered in a 12-mm precision-bore tube with the space between the tubes containing 97% by weight of acetone-d_6 for locking the field and 3% of triphenyl phosphite for referencing ^{31}P chemical shifts. In this paper the ^{31}P chemical shifts are all reported in terms of 85% H_3PO_4 using 128.1 ppm as the difference between the shift of triphenyl phosphite and 85% phosphoric acid. All protons were decoupled with "white-noise."

Magnetic susceptibility 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 magnesium(II) complex. The values obtained for the three Mg(II) complexes listed in Table I are 176×10^{-6}, 119×10^{-6}, and 735×10^{-6} cgsu.

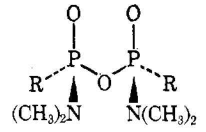
A conductance bridge manufactured by Industrial Instruments and equipped with a platinum dip-type cell (cell constant 0.110 cm⁻¹) was used to measure the conductance of nitromethane solutions of the complexes.

Results and Discussion

^{31}P Nmr of Ligands.—The ligands used in this study contain asymmetric phosphorus atoms. The proton-decoupled ^{31}P nmr spectrum of *P,P'*-diisopropyl-*N,N,-N',N'*-tetramethylpyrophosphoramide consists of two sharp peaks of equal intensity (Figure 1). We have assigned these to the racemic mixture (Ia) and to the meso form (Ib). This is the first report of a spectrum of this type for a P–O–P linkage although Maier[7] obtained similar spectra for the P–P linkage.



Ia, R = $CH(CH_3)_2$



Ib, R = $CH(CH_3)_2$

The same types of spectra have been observed for compounds where the isopropyl groups of I are replaced by methyl, ethyl, and ethoxy groups. The separation of the two peaks which we attribute to racemic and meso forms increases as the size of the substituent increases ($R = CH_3$, 5 Hz; $R = C_2H_5$, 7 Hz; $R = OC_2H_5$, 13.5 Hz; $R = CH(CH_3)_2$, 18 Hz, for spectra of neat liquids) and is also solvent dependent with larger values for the more basic solvents (2 Hz in nitromethane, 8.5 Hz in benzylamine). The possibility that the two peaks are caused by rotational isomers is eliminated by our observation that the decoupled ^{31}P nmr spectrum of the magnesium complex also consists of two peaks.

Characterization of Complexes.—Table I lists the analytical data, conductance data, and magnetic moments of the compounds which were isolated in this study. Abbreviations which will be used for the ligands of general formula $(R)[N(CH_3)_2]P(O)OP(O)[N(CH_3)_2](R)$ are M for $R = CH_3$, E for $R = C_2H_5$, and P for $R = i\text{-}C_3H_7$.

The 3:1 ratio of ligand to metal and the conductance data are evidence in support of chelation by the ligand to give six-coordinate metal ions. The electronic spectral data for Co(II) and Ni(II) complexes are typical of octahedral systems. Ligand field parameters calculated[8] for the Ni(II) complexes give *Dq* values of 730, 725, and 722 cm⁻¹ and β^0 values of 0.127, 0.133, and 0.130 for *P,P'*-dimethyl-, -diethyl-, and -diisopropyl-*N,N,N',N'*-tetramethylpyrophosphoramides, respectively. These values are similar to those obtained for the pyrophosphoryl group with other organic substituents attached to the phosphorus atoms.[1] The assignment of an octahedral configuration to Ni(II) is supported by the good agreement of the calculated and experimental values for the second band (12,340 *vs.* 12,500 cm⁻¹ for M; 12,266 *vs.* 12,195 cm⁻¹ for E; 12,182 *vs.* 12,145 cm⁻¹ for P). Except for the Cu(II)

---

(7) L. Maier, *J. Inorg. Nucl. Chem.*, **24**, 275 (1962).

(8) R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold, New York, N. Y., 1965, p 410.

TABLE II

ELECTRONIC SPECTRAL DATA[a]

Compound	λ_{max}, cm^{-1}	ϵ	Compound	λ_{max}, cm^{-1}	ϵ
$Co(M)_3(ClO_4)_2$	18,382	20	$Ni(E)_3(ClO_4)_2$	23,256	16
$Ni(M)_3(ClO_4)_2$	23,419	14		12,195	5
	12,500	5		7,246	4
	7,299	3	$Cu(E)_3(ClO_4)_2$	10,870	27
$Cu(M)_3(ClO_4)_2$	10,870	24	$Co(P)_3(ClO_4)_2$	18,939	21
$Co(E)_3(ClO_4)_2$	18,315	25	$Ni(P)_3(ClO_4)_2$	23,256	20
				12,195	6
				7,220	3
			$Cu(P)_3(ClO_4)_2$	10,870	41

[a] In nitromethane.

complexes, the magnetic moments are at the high end of the range expected for spin-free octahedral complexes [4.7–5.2 BM for Co(II), 2.9–3.4 BM for Ni(II), 1.7–2.2 BM for Cu(II)].

The P–O frequency decreased by about 10–40 cm^{-1} in the complexes, indicating coordination through the phosphoryl donor site. This is expected since X-ray diffraction studies[9] have shown that the coordination sites in octamethylpyrophosphoramide (OMPA) are the phosphoryl oxygen atoms rather than the dimethylamino nitrogen atoms.

Acknowledgments.—Portions of this research were supported by NIH-GM-15451-03. The Varian XL-100-15 spectrometer and the Faraday magnetic apparatus were purchased through Vanderbilt's "Centers of Excellence" award under the Science Development Program sponsored by the National Science Foundation and Vanderbilt University.

[9] M. D. Joesten, M. S. Hussain, and P. G. Lenhert, *Inorg. Chem.*, **9**, 151 (1970).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN 48104

Facile Syntheses of Germanium Dibromide, Hexabromodigermane, and Tribromomethyltribromogermane

BY M. DAVID CURTIS* AND PAUL WOLBER

Received June 1, 1971

Previously reported syntheses of germanium dibromide are the reactions of hydrogen bromide gas with germanium[1] and aqueous hydrogen bromide with germanium(II) hydroxide.[2] The first method produces a mixture of tribromogermane and germanium tetrabromide. Upon vacuum distillation, the tribromogermane decomposes into hydrogen bromide and germanium dibromide. Tribromogermane is also believed to be an intermediate in the second method.[2] Thus, the dibromide prepared by either method may contain traces of protonic impurities, and we sought a preparation which would eliminate these contaminants.

Germanium dichloride has been prepared from germanium and germanium tetrachloride,[3] and we now report a similar route to the dibromide utilizing germanium and either bromine or germanium tetrabromide. During the investigation, several new insertion reactions of germanium dibromide were also discovered.

Experimental Section

Germanium powder was obtained from the Eagle Pitcher Corp., Quapaw, Okla. Raman spectra were obtained on a Spex Ramalog laser unit with the Spex 1401 monochromator. The excitation wavelength was the 4880-Å line of Ar$^+$. Precession photographs of $GeBr_2$ were obtained using Cu Kα radiation. A piece of thin nickel foil was placed on the layer line screen to filter the white radiation. Standard Schlenk-tube techniques[4] were used to maintain inert atmospheres. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Germanium Dibromide.—Germanium powder was sprinkled onto glass wool loosely packed in a vertical Vycor tube (18-mm o.d.) wound with a heating element and covered with asbestos tape (Figure 1). The tube was packed by alternately adding thin layers of glass wool and germanium (*ca.* 0.1 g per layer). It is important that the metal be dispersed throughout the volume of the tube as evenly as possible. Bromine (twice the theoretical amount for $GeBr_2$) was placed in A (Figure 1), the

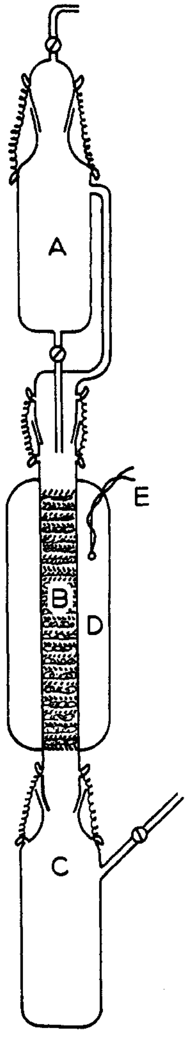


Figure 1.—Apparatus for the synthesis of germanium dibromide: A, constant-pressure dropping funnel; B, germanium powder dispersed on Pyrex wool; C, Schlenk tube; D, heating elements and insulation; E, thermocouple leads.

---

[1] F. M. Brewer and L. M. Dennis, *J. Phys. Chem.*, **31**, 1526 (1927).

[2] T. K. Gar and V. F. Mironov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 855 (1965).

[3] L. M. Dennis, W. R. Orndorff, and D. L. Tabern, *J. Phys. Chem.*, **30**, 1050 (1926).

[4] D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1968.