believe to be $[Ru(NH_3)_5NCH]^{2+}$. Our results and those described by Ford differ on the matter of the infrared absorption of the solid. Ford reports for the solid purported to be $[Ru(NH_3)_5NCH](ClO_4)_2$ a strong broad band at 1960 cm^{-1} which according to our observations represents a late decomposition product of I. We take the intermediate species which has a sharp maximum at 2020 cm^{-1} arising from I on aging of the solid to be the C-bound HCN complex, and, on the basis of results to be described, the material giving the broad final absorption (Figure 1d) to be a polynuclear CN$^-$-bridged species arising from the decomposition reaction

$$n[(NH_3)_5RuCNH](PF_6)_2 = [(NH_3)_4RuCN]_n[PF_6]_n + nNH_4PF_6 \quad (1)$$

Species I is unstable in solution and its decomposition (as measured by the disappearance of the band at 229 nm) accelerates as the acidity decreases. Approximate values for the specific rate of this reaction as a function of pH (acetate buffer) are: $k_{obsd} \times 10^2$, sec^{-1} = 1, 4, 7, 17, >70 at pH's of 3.6, 4.5, 4.8, 5.5, 7.0, respectively. We take the decomposition reaction, at least in its first stages, to involve isomerization of N-bound[4] HCN to a C-bound form, a reaction which it is reasonable to suppose will take place more readily for the deprotonated ligand than for the protonated.

When the reaction is studied with isonicotinamide (isn) present, the reaction course is simple, and a product is formed which has an absorption maximum at 415 nm. Similar absorption spectra were obtained for *trans*-$[Ru(NH_3)_4CN(isn)]^+$ starting with $[Ru(NH_3)_5NCH]^{2+}$ or $[Ru(NH_3)_5CN]^+$ and isonicotinamide at pH 8.3. Since $[Ru(NH_3)_5(isn)]^{2+}$ has a maximum at 480 nm, the reaction leading to product is not substitution of CN$^-$ by isn. From the kinetic behavior and in analogy to observations[1a] made on the labilization of trans ammonia by C-bound imidazole, we take the reaction product to be *trans*-$[Ru(NH_3)_4CN(isn)]^+$ (II).

The rate of formation of II from I was found to be independent of pH in the range 5 to 7.3, and of [isn] over the range 0.01 to 0.1 *M*. The specific rate calculated for the reaction is 5.3×10^{-3} sec^{-1}. The results just described, compared with those on rearrangement, show that the formation of the isn product is slow compared with the rearrangement of cyanide. We conclude, therefore, that the step governing the rate of formation of II is the release of trans NH_3 from the C-bound form of $Ru(NH_3)_5CN^+$. Comparison with the literature value[5] for the release of NH_3 from $Ru(NH_3)_6^{2+}$ shows that replacing NH_3 by CN$^-$ enhances the rate of trans ammonia release by a factor of 3×10^3. The effect of CN$^-$ is almost as great as that of SO_3^{2-} where the corresponding labilizing factor is found[6] to be 6×10^3.

Aging the solid for a period of days or adding I to ~2 *M* NH_3 and immediately reprecipitating it produced spectrum 1d. In view of the labilization of the trans position noted above, it is reasonable to suppose that the substance giving rise to 1d is the product of polymerization of $Ru(NH_3)_4CN^+$. An analysis was not obtained for the solid, but the conclusion that the species is polymeric is supported by the fact that it is not eluted from a cation exchange column by 1.5 *M* LiCl. For this interpretation to be accepted, a great decrease in the affinity of NH_3 for Ru(II) when CN$^-$ is coordinated must be assumed, in line with the increased lability already documented for the trans ammonia.

An incidental conclusion which follows from the rate profiles, *k* vs. pH, for the decomposition (rearrangement) reaction and the formation of II is that while $Ru(NH_3)_5NCH^{2+}$ is still largely protonated at pH 5.5, $Ru(NH_3)_5CNH^{2+}$ is fully deprotonated at this pH.

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Registry No. $[Ru(NH_3)_5(H_2O)]^{2+}$, 21393-88-4; $[Ru(NH_3)_5(NCH)](PF_6)_2$, 55822-60-1; $[Ru(NH_3)_5CN]PF_6$, 55822-62-3; *trans*-$[Ru(NH_3)_4CN(isn)]^+$, 55822-63-4.

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The Hydrolysis of Methyl(phosphino)germanes. Evidence for Ge–H Bond Lability in Methylgermoxanes[1]

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It has been reported that instead of rapidly cleaving the germanium–phosphorus bond of GeH_3PH_2 to form phosphine and germanol and/or germoxane products, water promotes the redistribution of germyl and hydrido groups on phosphorus to yield phosphine, digermylphosphine, and trigermylphosphine.[3] Prompted by our interests in redistribution reactions as routes to new germanium–phosphorus bonded compounds[4–6] we have examined reactions that the methyl(phosphino)germanes, $(CH_3)_2Ge(PH_2)H$, $(CH_3)_2Ge(PH_2)_2$, and $(CH_3)_3GePH_2$, undergo with water. Our results are reported below.

Experimental Section

Apparatus and Materials. All manipulations were carried out in standard vacuum-line apparatus.[7] Proton magnetic resonance data were obtained using a Varian A-60A spectrometer. Proton chemical shift values are reported relative to internal $(CH_3)_4Si$ (negative δ downfield). Infrared spectra were obtained with a Perkin-Elmer Model 337-G spectrometer. Mass spectra were obtained with a Varian MAT CH-5 spectrometer operating at an ionizing voltage of 70 eV. The $(CH_3)_2Ge(PH_2)H$, $(CH_3)_2Ge(PH_2)_2$, and $(CH_3)_3GePH_2$ were prepared as described previously.[8] Dimethoxyethane (monoglyme) was distilled from $LiAlH_4$ prior to use. Distilled water was used in hydrolysis reactions.

Hydrolysis Reactions. Typically, the methyl(phosphino)germanes and water, and in some cases monoglyme, were condensed into heavy-walled NMR tubes or Pyrex bulbs and allowed to react as shown in Table I. Examples in the table are bulb reactions unless specified otherwise. Products from bulb reactions were removed and separated by fractional condensation and/or sublimation techniques. Reaction materials were identified by comparison of their reported spectral properties with literature values as: PH_3 (ir[9] and ^1H NMR[10]), $(CH_3)_2GeH_2$ (ir[11] and ^1H NMR[12]), $(CH_3)_2Ge(PH_2)H$ (^1H NMR[8]), $(CH_3)_2Ge(PH_2)_2$ (^1H NMR[8]), $(CH_3)_3GePH_2$ (^1H NMR[8]), $[(CH_3)_3Ge]_2O$ (^1H NMR[13]), and $[(CH_3)_2GeO]_{3,4}$ (^1H NMR[14]). In experiments 2 and 3, the reported quantities of $[(CH_3)_2GeO]_{3,4}$ are those obtained after purification of the products by sublimation along a horizontal gradient-heated sublimation tube. The $[(CH_3)_2GeH]_2O$ in experiment 4 was separated crudely from other reactants by fractional condensation. Extraction of the crude material into diethyl ether followed by removal of the ether in vacuo resulted in pure $[(CH_3)_2GeH]_2O$ in about 50% yield.

In a separate series of experiments, $(CH_3)_2Ge(PH_2)H$ and H_2O in a 10:1 ratio in monoglyme in an NMR tube were allowed to react at room temperature while reaction progress was periodically

Table I. Typical Hydrolysis Data[a]

Expt. No.	Reactants (mmol)	Time	Products (mmol)
1[b]	$(CH_3)_3GePH_2$ (0.4)[c] H_2O (0.04)	72 hr	$[(CH_3)_3Ge]_2O$ (0.04) PH_3 (nm)[d]
2	$(CH_3)_2Ge(PH_2)_2$ (1.0) H_2O (ca. 5)	12 hr	$[(CH_3)_2GeO]_{3,4}$ (0.74)[e] PH_3 (2.0)
3	$(CH_3)_2Ge(PH_2)H$ (1.06) H_2O (ca. 5)	12 hr	$(CH_3)_2GeH_2$ (0.51) $[(CH_3)_2GeO]_{3,4}$ (0.50)[e] PH_3 (1.04)
4	$(CH_3)_2Ge(PH_2)H$ (1.0)[c] H_2O (0.3)	100 min	$[(CH_3)_2GeH]_2O$ (0.15) $(CH_3)_2GeH_2$ (0.14) $[(CH_3)_2GeO]_{3,4}$ (0.12)[e] PH_3 (0.58)

[a] All reactions carried out at 25 ± 2°. [b] Reaction in monoglyme solvent in heavy-walled NMR tube. [c] Reactant in excess. [d] Quantity not measured. [e] Quantity in parentheses expressed in millimoles of $(CH_3)_2GeO$ units.

monitored by examining the ^1H NMR spectra. Within minutes, resonances due to $[(CH_3)_2GeH]_2O$ and PH_3 appeared. Over a period of days the excess $(CH_3)_2Ge(PH_2)H$ underwent redistribution on germanium to form $((CH_3)_2Ge(PH_2)_2$ and $(CH_3)_2GeH_2$.[6] Eventually the $[(CH_3)_2GeH]_2O$ resonances disappeared and resonances due to $[(CH_3)_2GeO]_3$ and $[(CH_3)_2GeO]_4$ at δ −0.49 and −0.47 ppm appeared and the solid products characteristic of $(CH_3)_2Ge(PH_2)_2$ condensation[4,5] began to form.

Characterization of $[(CH_3)_2GeH]_2O$. Decomposition of $[(CH_3)_2GeH]_2O$ for elemental analysis was effected by its reaction with excess HBr. The ratio of $[(CH_3)_2GeH]_2O$:$(CH_3)_2GeHBr$ according to

$$[(CH_3)_2GeH]_2O + 2HBr \rightarrow 2(CH_3)_2GeHBr + H_2O \qquad (1)$$

is: calcd, 1.00:2.00; found, 1.00:1.93.

Infrared spectral absorptions occur at: 3000 (s), 2940 (m), 2880 (m), 2070 (s), 2050 (vs), 1425 (w), 1380 (w), 1370 (w), 1325 (w), 1225 (m), 1140 (m), 850 (s), 820 (vs), 760 (m), 700 (s), 615 (s), and 595 (m) cm^{-1}. The most intense peak in the six most intense mass spectral envelopes occurs at m/e (% abundance): 223 (20.7), 209 (47.6), 193 (10.5), 119 (100), 105 (48.4), and 89 (40.3). The m/e 223 envelope arises from $(CH_3)_4Ge_2OH^+$ (parent minus one H) ions. The ^1H NMR spectrum shows resonances in diethyl ether solvent at (relative area; peak multiplicity): δ −0.13 (12; 2) and −5.45 ppm (2; 7), assignable to $(CH_3)_2Ge$ and GeH protons, respectively, with $^3J_{HCGeH} = 2.0 \pm 0.1$ Hz.

The $[(CH_3)_2GeH]_2O$ has a 0° vapor tension of ca. 10 Torr; however, thermal instability precluded complete vapor tension vs. temperature measurements.

Exposure of a sample of $[(CH_3)_2GeH]_2O$ to ambient air for 12 hr resulted in its quantitative conversion to $[(CH_3)_2GeO]_{3,4}$ species. In the absence of air and traces of water, a sample of $[(CH_3)_2GeH]_2O$ in diethyl ether in an NMR tube showed slight decomposition during 4 hr at 32°.

Results and Discussion

At ambient temperatures water reacts with $(CH_3)_2Ge(PH_2)_2$, $(CH_3)_2Ge(PH_2)H$, and $(CH_3)_3GePH_2$, cleaving the germanium–phosphorus bonds to form phosphine and methylgermoxane products according to a reaction which can be described generally as

$$2(\equiv Ge{-}PH_2) + H_2O \rightarrow (\equiv Ge)_2O + 2PH_3 \qquad (2)$$

The $[(CH_3)_3Ge]_2O$[13] and $[(CH_3)_2GeO]_{3,4}$[14] species were obtained from $(CH_3)_3GePH_2$ and $(CH_3)_2Ge(PH_2)_2$ hydrolyses, respectively, in essentially quantitative yields. These reactions are analogous to those of completely substituted (organophosphino)alkylgermanes which have been reported previously.[15] No evidence for the occurrence of redistribution-on-phosphorus reactions occurring at rates equal to or faster than hydrolysis reactions was obtained in any of the reaction systems studied. These observations are in contrast with those reported for GeH_3PH_2 by Drake and Riddle[3] and may indicate that the methyl groups have a moderating effect on redistribution-on-phosphorus reactions relative to hydrolysis reactions in the methyl(phosphino)germanes. Also, under our reaction conditions no evidence for germanol ($\equiv$GeOH) or digermanol ($>Ge(OH)_2$) species as reaction intermediates was obtained, as has been reported in the hydrolysis of some alkyl(halo)germanes.[15]

The reactions of $(CH_3)_2Ge(PH_2)H$ with water are somewhat more complex than those of $(CH_3)_3GePH_2$ and $(CH_3)_2Ge(PH_2)_2$ due to the presence of the relatively labile Ge–H bond in the system. Long reaction times (>2 hr) and the presence of excess water lead to the exclusive formation of $(CH_3)_2GeH_2$, PH_3, and $[(CH_3)_2GeO]_{3,4}$. Our data allow the reaction stoichiometry to be expressed as

$$2n(CH_3)_2Ge(PH_2)H + nH_2O \rightarrow [(CH_3)_2GeO]_n + 2nPH_3 + n(CH_3)_2GeH_2 \qquad (3)$$

However, a shorter reaction period (20–100 min) and a deficiency of water result in formation of $[(CH_3)_2GeH]_2O$, along with PH_3, $(CH_3)_2GeH_2$, and $[(CH_3)_2GeO]_{3,4}$.

The $[(CH_3)_2GeH]_2O$ probably arises through the direct hydrolysis reaction shown in eq 2. The instability of $[(CH_3)_2GeH]_2O$ under our reaction conditions is surprising, since similar instability for the $[R_2GeH]_2O$ products obtained from hydrolyses of diethylhydrogermyl and dibutylhydrogermyl halides was not reported. The $[(CH_3)_2GeH]_2O$ undergoes a redistribution of groups on germanium as

$$n[(CH_3)_2GeH]_2O \rightarrow [(CH_3)_2GeO]_n + n(CH_3)_2GeH_2 \qquad (4)$$

in a manner analogous to what may occur with the redistribution of hydrogen and phosphino groups,[6,16] hydrogen and selenogermyl groups,[17] and hydrogen and halide atoms on germanium atom[18] centers. Excess water appears to appreciably accelerate the rate of the redistribution of groups in $[(CH_3)_2GeH]_2O$, since dry samples of $[(CH_3)_2GeH]_2O$, neat or in ether, showed only slight reaction in periods of several hours. The possibility that with $(CH_3)_2Ge(PH_2)H$ the redistribution of PH_2 and H groups to yield $(CH_3)_2GeH_2$ and $(CH_3)_2Ge(PH_2)_2$ occurs prior to or simultaneous with hydrolysis of $(CH_3)_2Ge(PH_2)H$ can be considered. After this the $(CH_3)_2Ge(PH_2)_2$ undergoes hydrolysis to form the $[(CH_3)_2GeO]_{3,4}$ species. However, this seems unlikely since (1) in hydrolyses carried out in NMR tubes no evidence for $(CH_3)_3GeH_2$ formation was seen until after the $[(CH_3)_2GeH]_2O$ had formed and begun to disappear and (2) in separate experiments the $(CH_3)_2Ge(PH_2)_2$ hydrolysis was found to be relatively slow.

Registry No. $(CH_3)_3GePH_2$, 20519-92-0; $(CH_3)_2Ge(PH_2)_2$, 20519-93-1; $(CH_3)_2Ge(PH_2)H$, 26465-28-1; $[(CH_3)_2GeH]_2O$, 33129-30-5.

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Magnetic Properties of Tetraaquo-bis(μ-hippurato-*O*)-bis(hippurato-*O*)dicopper(II) Tetrahydrate

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In recent years there has been much interest in the correlation between the structural features and the magnetic properties of bridged copper(II) dimers. Several groups have postulated such correlations,[1] both qualitative and quantitative, for the cases where the geometry around the copper atom is tetragonal pyramidal or square planar and the bridging atom (frequently oxygen) is in the basal (*xy*) plane. In these cases the orbitals containing the unpaired spin (which lie in the *xy* plane) overlap well with the bridging orbitals. The concepts which have been used successfully in these cases, however, are not applicable in the case of the parallel-planar copper(II) dimers,[2] in which the bridging atom occupies an in-plane coordination site on one copper(II) ion and an apical site of the other copper(II) ion, or in the case of the paired trigonal-bipyramidal systems. In both of these latter situations the molecules can be envisaged as pyramids or bipyramids which share an equatorial-to-apical edge.[3] For these geometries, the overlap is very different; in the extreme case for which the Cu–L–Cu angle is 90°, the s and p orbitals on the bridging atom are orthogonal to the orbital on one copper which contains the unpaired spin. Hence, for such systems the magnitude of the singlet–triplet splitting, $2J$, should be much smaller than in the previous examples, and this has been demonstrated for some 2:1 pyridine-*N*-oxide–copper(II) dimers. In both bis[dinitratobis(pyridine-*N*-oxide)copper(II)], $[Cu(pyO)_2(NO_3)_2]_2$,[4] and bis[dinitratobis(4-methoxypyridine-*N*-oxide)copper(II)], $[Cu(4\text{-}MeOpyO)_2(NO_3)_2]_2$,[5] the bridging oxygen atoms are in apical positions and the $2J$ values measured are $+10\ cm^{-1}$ [6] and $-2\ cm^{-1}$,[7] respectively.

The compound tetraaquo-bis(μ-hippurato-*O*)-bis(hippurato-*O*)dicopper tetrahydrate, $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2 \cdot 4H_2O$,[8] has distorted [4 + 1] tetragonal-pyramidal geometry and is bridged through two carboxyl oxygen atoms of the hippurate ions. Each bridging oxygen atom simultaneously occupies an equatorial position on one copper atom and an apical position on the other copper atom in the dimer; the Cu–O–Cu angle is 101.0°. It appeared, therefore, that the magnitude of $2J$ for this compound should also be small. To test this hypothesis and to gain further understanding of the magnetic properties of compounds of this structural type, we have obtained magnetic susceptibility data in the range 1.7–121° for this complex and have determined the value of the singlet–triplet splitting. The results of these studies are reported herein.

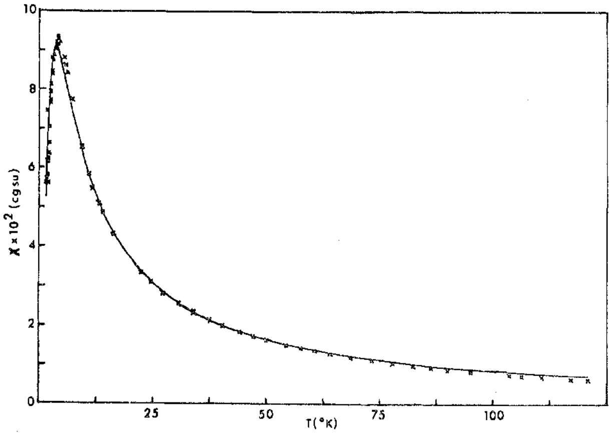

Figure 1. Plot of the magnetic susceptibility of $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2 \cdot 4H_2O$ per dimer as a function of temperature. The solid line represents the values calculated from the magnetization expression with $g = 2.13$, $2J = -4.3\ cm^{-1}$, and $\gamma = -1.9$.

Experimental Section

Preparation. The complex $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2 \cdot 4H_2O$ was prepared by the method of Brown et al.[9] The light blue crystals obtained gave satisfactory analyses.

Magnetic Measurements. Magnetic susceptibility measurements were made on a powdered sample of $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2 \cdot 4H_2O$ using a Foner-type vibrating-sample magnetometer[10] operating at 10 kG as described elsewhere.[11] Mercury tetrathiocyanatocobaltate(II)[12] was used as a susceptibility standard. Measurements were made in the temperature range 1.7–121°K. The temperatures were measured with a calibrated Ga–As diode. Above 4.2°K and below 10,000 G the diode is independent (<0.01°K) of the field strength. Below 4.2°K the diode becomes field dependent, but recent careful measurements[13] on $[Cu(2,2'\text{-}bpy)_2(tu)](ClO_4)_2$ indicate that the error is not excessive since the data for this magnetically dilute system obey the Curie–Weiss law to 1.6°K with $\Theta = -0.020°K$. Susceptibilities were corrected for the diamagnetism of the substituent atoms using Pascal's constants[14] and for the temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60×10^{-6} cgsu/Cu atom).

Results and Discussion

The temperature variation of the magnetic susceptibility of $[Cu[(C_6H_5)CONHCH_2COO]_2(H_2O)_2]_2 \cdot 4H_2O$ is plotted in Figure 1. A maximum in this plot is observed at approximately 4°K, and the data are approximated by the Bleaney–Bowers equation[15]

$$\chi_m = \frac{Ng^2\beta^2}{3k(T-\Theta)}[1 + {}^1/_3 \exp(-2J/kT)]^{-1} \qquad (1)$$

The best least-squares fit of the data to this equation with $\Theta = 0.0°$ gives a singlet–triplet splitting, $2J$, of $-4.3\ cm^{-1}$ with $g = 1.97$; the mean fractional deviation (MFD), defined as $\sum[(|\chi_{obsd} - \chi_{calcd}|)/\chi_{obsd}]/NO$, where NO is the number of observations (68 in the present case), of a data point from the theoretical curve is 0.074. The inclusion of the interdimer interaction parameter θ improves the fit considerably, yielding a $2J$ value of $-3.2\ cm^{-1}$ with $g = 2.14$ and $\Theta = -2.2°$ and lowering the MFD to 0.043.

However, the small value of $2J$ obtained indicates that eq 1 may not be appropriate since in the Bleaney–Bowers equation the approximation is made that $2J >> g\beta H$; for $H = 10$ kG, $g\beta H = 1.0\ cm^{-1}$. For cases where $2J$ is of the same order of