

TABLE III  
POSITIONAL AND THERMAL PARAMETERS FOR CsEu(HFA)<sub>4</sub>  
(TOP) AND CsAm(HFA)<sub>4</sub> (BOTTOM) AND  
THEIR STANDARD ERRORS<sup>a</sup>

Atom	x	y	z	10 <sup>3</sup> B <sub>11</sub> <sup>a</sup>	10 <sup>3</sup> B <sub>22</sub>	10 <sup>3</sup> B <sub>33</sub>	10 <sup>3</sup> B <sub>12</sub>	10 <sup>3</sup> B <sub>13</sub>	10 <sup>3</sup> B <sub>23</sub>
Cs	0.5(0) <sup>b</sup>	0.2695(7)	0.25(0)	118(2)	41(2)	66(1)	0(0)	2(2)	0(0)
Eu	0.0(0)	0.3165(4)	0.25(0)	89(1)	19(1)	46(1)	0(0)	2(1)	0(0)
O1	-0.221(1)	0.3569(5)	0.3179(6)	93(16)	30(3)	45(5)	-3(7)	18(7)	0(3)
O2	0.084(1)	0.4009(6)	0.3246(7)	109(17)	36(4)	60(6)	2(7)	-9(9)	0(4)
O3	-0.139(1)	0.2308(5)	0.3302(7)	127(18)	21(3)	54(5)	7(6)	3(8)	-6(3)
O4	0.152(1)	0.2745(5)	0.3495(6)	194(21)	30(3)	43(5)	-21(7)	-15(9)	12(4)
F1	-0.427(2)	0.4449(9)	0.437(1)	197(22)	106(8)	154(12)	13(11)	60(13)	93(9)
F2	-0.488(2)	0.3671(7)	0.386(2)	259(30)	65(6)	389(25)	82(13)	213(25)	75(11)
F3	-0.481(2)	0.4397(13)	0.331(1)	152(26)	202(16)	140(11)	-121(19)	73(14)	-86(11)
F4	0.220(2)	0.4731(6)	0.438(1)	264(26)	60(5)	107(9)	-15(9)	-53(13)	-30(5)
F5	0.212(2)	0.5139(6)	0.332(1)	502(36)	55(5)	100(9)	-120(12)	74(15)	-13(5)
F6	0.055(1)	0.5395(5)	0.412(1)	194(22)	40(3)	190(12)	0(7)	-3(12)	-4(5)
F7	-0.219(2)	0.1045(10)	0.410(2)	613(55)	108(9)	158(14)	190(19)	-115(22)	-92(11)
F8	-0.194(3)	0.0969(9)	0.299(1)	846(88)	77(7)	186(18)	184(24)	86(28)	55(10)
F9	-0.347(1)	0.1593(7)	0.339(2)	195(126)	37(5)	382(26)	52(9)	-37(23)	-67(9)
F10	0.251(2)	0.2462(14)	0.509(1)	339(35)	201(16)	89(10)	60(17)	-85(18)	-46(10)
F11	0.406(2)	0.2399(9)	0.420(1)	157(22)	148(11)	127(10)	-46(13)	-60(13)	96(9)
F12	0.297(2)	0.1642(7)	0.459(1)	613(55)	347(31)	65(6)	153(13)	-12(12)	-115(17)
O1	-0.409(2)	0.4093(14)	0.386(2)	105(14)	54(10)	131(19)	-60(16)	-54(22)	55(12)
O2	-0.242(2)	0.4050(8)	0.359(1)	157(30)	26(5)	36(7)	-25(10)	37(12)	-4(5)
O3	-0.138(2)	0.4515(7)	0.378(1)	135(30)	18(4)	58(8)	4(10)	-2(13)	-1(5)
O4	0.016(2)	0.4426(8)	0.360(1)	168(37)	26(5)	56(8)	32(16)	-7(19)	1(5)
O5	0.127(2)	0.4952(10)	0.384(1)	191(37)	24(6)	78(13)	-3(14)	19(19)	6(7)
O6	-0.211(3)	0.1347(16)	0.353(2)	256(54)	63(11)	111(19)	92(22)	-45(26)	-4(13)
O7	-0.099(2)	0.1881(9)	0.346(1)	100(32)	28(6)	76(12)	29(13)	28(15)	18(7)
O8	0.032(2)	0.1781(8)	0.391(1)	131(41)	26(4)	64(9)	17(10)	8(13)	-9(6)
O9	0.144(2)	0.2271(8)	0.308(1)	145(30)	34(6)	36(8)	-3(12)	0(13)	1(6)
O10	0.282(4)	0.2215(15)	0.446(2)	357(66)	51(9)	60(12)	21(22)	8(27)	40(10)
Cs	0.5(0)	0.26803(9)	0.25(0)	121(4)	38(1)	63(1)	0(0)	1(3)	0(0)
Am	0.0(0)	0.31633(4)	0.25(0)	88(2)	16(1)	43(1)	0(0)	3(2)	0(0)
O1	-0.227(2)	0.3554(6)	0.3155(8)	105(26)	20(4)	32(7)	7(9)	9(12)	4(5)
O2	0.080(2)	0.3998(7)	0.3295(8)	108(25)	28(4)	49(8)	-5(9)	12(12)	-30(5)
O3	-0.141(2)	0.2294(7)	0.3048(9)	83(28)	33(5)	48(8)	18(9)	-18(12)	-11(6)
O4	0.156(2)	0.2735(7)	0.3512(9)	140(31)	23(5)	45(8)	0(9)	-39(13)	-5(5)
F1	-0.432(2)	0.443(1)	0.435(2)	150(32)	112(11)	138(16)	12(14)	48(18)	77(13)
F2	-0.490(3)	0.367(1)	0.391(2)	318(43)	54(6)	293(30)	51(18)	217(34)	45(12)
F3	-0.484(3)	0.440(2)	0.333(2)	192(39)	236(23)	107(14)	-122(29)	45(25)	-75(15)
F4	0.216(2)	0.476(1)	0.435(1)	250(34)	49(6)	112(13)	-16(11)	-33(20)	-25(7)
F5	0.198(3)	0.515(1)	0.332(1)	588(58)	49(6)	100(12)	-128(17)	79(25)	-23(7)
F6	0.047(2)	0.540(1)	0.419(1)	185(36)	39(5)	167(15)	-16(9)	13(18)	-40(7)
F7	-0.213(3)	0.103(1)	0.406(2)	625(77)	110(12)	167(21)	196(27)	-181(34)	-97(15)
F8	-0.102(4)	0.098(1)	0.302(2)	794(105)	64(9)	180(24)	166(27)	66(39)	33(13)
F9	-0.348(2)	0.149(1)	0.344(3)	225(44)	42(7)	419(40)	37(11)	-66(15)	-68(14)
F10	0.256(3)	0.243(2)	0.504(2)	425(60)	138(13)	116(14)	54(22)	-97(27)	-39(13)
F11	0.414(2)	0.235(1)	0.423(1)	158(30)	130(12)	113(14)	-48(17)	-74(20)	70(11)
F12	0.305(2)	0.161(1)	0.466(2)	337(44)	84(10)	216(24)	-7(17)	-173(28)	64(14)
O1	-0.419(5)	0.411(2)	0.381(3)	8.0(10) <sup>c</sup>					
O2	-0.241(3)	0.405(1)	0.354(2)	4.2(6)					
O3	-0.142(3)	0.449(1)	0.377(2)	4.2(6)					
O4	0.022(3)	0.441(1)	0.359(2)	3.4(5)					
O5	0.113(4)	0.494(2)	0.383(2)	7.5(8)					
O6	-0.225(5)	0.138(2)	0.350(3)	9.1(10)					
O7	-0.096(3)	0.188(1)	0.350(2)	4.9(6)					
O8	0.034(2)	0.177(1)	0.392(1)	4.1(5)					
O9	0.142(3)	0.225(1)	0.350(2)	5.6(7)					
O10	0.285(6)	0.214(2)	0.442(3)	10.7(11)					

<sup>a</sup> Numbering scheme is the same as that of Bennett, *et al.*,<sup>5</sup> and agrees with that in Figure 1.

	TABLE IV		
	M = Y	M = Eu	M = Am
	Distance Errors, Å		
M-O	0.01	0.01	0.02
C-O	0.02	0.02	0.03
C-C	0.02	0.02	0.03
C-F	0.03	0.04	0.05
	Angle Errors, Deg		
O-M-O	0.3	0.4	0.7
M-O-C	0.7	1.0	1.5
O-C-C	1.0	2.0	2.0
C-C-C	1.0	2.0	3.0

polyhedron consisting of these 12 neighbors is the twofold crystallographic axis passing through the Cs<sup>+</sup> ion. The fact discussed by the previous authors that between chains there are only F...F contacts is also apparent in Figure 2.

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## Proton Magnetic Resonance Studies of Phosphoryl Transition Metal Compounds

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The coordination properties of dimethyl methylphosphonate, DMMP = (CH<sub>3</sub>)<sub>2</sub>P(O)(OCH<sub>3</sub>)<sub>2</sub>, and trimethyl phosphate,<sup>2</sup> TMP = (O)P(OCH<sub>3</sub>)<sub>3</sub>, have been investigated. The proton spin-spin relaxation times (*T*<sub>2</sub>) and the phosphorus spin-lattice relaxation times (*T*<sub>1</sub>) of compounds of the type M(L)<sub>x</sub>(ClO<sub>4</sub>)<sub>2</sub> (M is an iron series transition metal, L is a phosphoryl ligand, and *X* is the coordination number) have been examined in neat solutions of the ligands in an effort to study the ligand-exchange reactions.

The hexamethylphosphoramide, HMPA = (O)P(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>, complexes were prepared as previously described.<sup>3</sup> A similar procedure was used to prepare the DMMP and TMP complexes. Dehydration of M(H<sub>2</sub>O)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> with triethyl orthoformate was followed by the addition of a slight excess of ligand. The complexes were precipitated, as oils, upon the addition of diethyl ether. Solids were obtained by repeated washing with fresh ether. The solids were dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>. The compounds isolated are shown in Table I. This procedure did not give pure solids in the following cases: DMMP with Fe<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup>; TMP with Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup>; and dimethyl hydrogen phosphite, DHP = (H)P(O)(OCH<sub>3</sub>)<sub>2</sub>, with the entire iron series.

All solutions were made in a nitrogen atmosphere. The nmr data were obtained on a Varian A-60 spectrometer. The effective magnetic moments were determined by the method of Evans<sup>4</sup> using benzene as an inert reference in a solution of the ligand. Infrared spectra were obtained on a 521 Perkin-Elmer grating spectrometer (Nujol on CsI plates). The concentration of complex used to obtain the relaxation time data was: Co(HMPA)<sub>4</sub><sup>2+</sup>, (0.67-1.6) × 10<sup>-2</sup> M; Fe(HMPA)<sub>4</sub><sup>2+</sup>, (0.45-1.3) × 10<sup>-2</sup> M; Mn(HMPA)<sub>4</sub><sup>2+</sup>, (0.12-3.1) × 10<sup>-2</sup> M; Mn(DMMP)<sub>6</sub><sup>2+</sup>, (0.14-7.2) × 10<sup>-2</sup> M; Mn(TMP)<sub>6</sub><sup>2+</sup>, (2.0-5.3) × 10<sup>-2</sup> M.

The infrared phosphoryl shifts (Table I) clearly show that coordination involves the phosphoryl group. As is typical Fe<sup>3+</sup> gives a much larger shift than Mn<sup>2+</sup>. The analytical data are tabulated in Table I as are the effective magnetic moments (*μ*). HMPA, diisopropyl methylphosphonate,<sup>5</sup> and triphenyl phosphine oxide<sup>6</sup>

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TABLE I  
 METAL SALT COMPLEXES OF DMMP AND TMP

Complex	Color	$\nu(\text{P}=\text{O})^a$ cm <sup>-1</sup>	$\mu$ , BM	Analysis, %									
				Calcd				Found					
				C	H	Cl	M	P	C	H	Cl	M	P
Mn(DMMP) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	White	1200	5.9	21.7	5.4	7.1	5.5	18.6	21.3	5.4	6.8	5.7	18.6
Fe(DMMP) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	White	1175	<i>c</i>	19.7	5.0	9.7	5.1	16.9	19.8	5.2	9.5	5.2	16.9
Cu(DMMP) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	Green	<i>b</i>	1.7	19.0	4.8	9.4	8.4	16.3	18.7	4.8	9.5	8.5	16.1
Mn(TMP) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	White	1260	5.9	19.8	5.0	6.5	5.0	17.0	19.9	5.0	6.3	5.0	16.9
Fe(TMP) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	White	1200	<i>c</i>	18.1	4.6	8.9	4.7	15.6	17.8	5.1	9.3	5.0	15.6

<sup>a</sup> DMMP, 1242 cm<sup>-1</sup>; TMP, 1280 cm<sup>-1</sup>. <sup>b</sup> Reacts with CsI plates. <sup>c</sup> Not sufficiently soluble.

form four-coordinate complexes with Mn<sup>2+</sup> as does the latter ligand with Fe<sup>3+</sup>. These results strongly suggest that steric considerations are a primary factor in determining the coordination numbers of phosphoryl ligands. Wayland and Drago<sup>3</sup> have shown that in a solution of HMPA all metal complexes are tetrahedral with the exception of Ni(II). The proton contact shifts of the HMPA complexes and their temperature dependence has also been reported.<sup>3</sup> The solution magnetic moments (Table I) and color (water white) of the Mn(II) complexes of DMMP and TMP are consistent with an octahedral structure.

The methyl proton signals of the neat ligands are doublets due to spin-spin coupling with the phosphorus nucleus. The proton spectra of various phosphoryl ligands in dilute solutions of paramagnetic metals exhibit spin multiplet collapse due to rapid phosphorus nuclear spin isomerization by the paramagnetic metal.<sup>7,8</sup> A typical set of spectra is given in Figure 1.

Phosphorus decoupling in the proton spectrum is unlikely to originate from a second sphere interaction. Zumdahl and Drago<sup>9</sup> have studied ligand-exchange reactions of Co(HMPA)<sub>2</sub>(X)<sub>2</sub> (X = halogen) in excess HMPA. At low temperature, separate peaks for free and bound ligand are observed. The heteronuclear double-resonance experiment definitively shows that the free ligand does not undergo chemical spin decoupling. Experiments with DHP and DMMP with nonlabile Cr(III) compounds (Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>, Cr(en)<sub>3</sub><sup>3+</sup>, Cr(SCN)<sub>6</sub><sup>3-</sup>), where the relaxation times must be second sphere in nature, show no evidence of chemical spin decoupling. These results may readily be explained by considering the second-sphere relaxation mechanism. Owing to the rapid attenuation with distance of the hyperfine coupling constant all second-sphere relaxation times will be dipole-dipole in nature.<sup>10</sup> Relative dipole-dipole relaxation rates are proportional to the squares of the gyromagnetic ratio ( $\gamma^2$ ) and the inverse sixth-power dependence of the distance from the metal to the nucleus under consideration ( $r^{-6}$ ).<sup>11</sup> The gyromagnetic ratio effect,  $(\gamma_{\text{H}}/\gamma_{\text{P}})^2 = 6.1$ , favors proton relaxation rates which are faster than phosphorus relaxation rates in the second coordination sphere. The gyromagnetic ratio effect may be somewhat offset by second-sphere orienta-

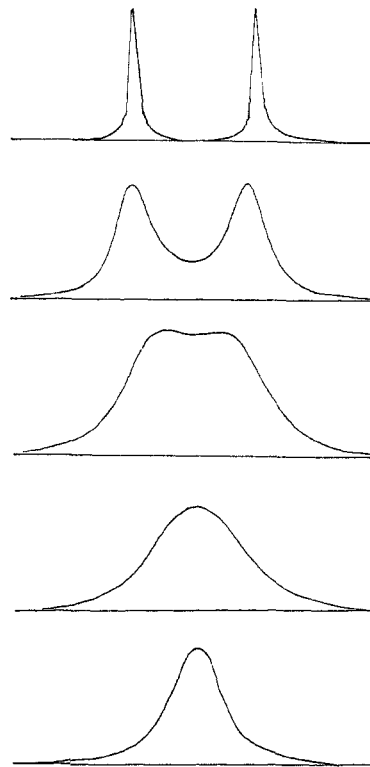


Figure 1.—The methyl signals of HMPA as a function of concentration of Co(HMPA)<sub>4</sub><sup>2+</sup> at 38°, the concentration of Co(II) being varied to 0.016 M.

tion effects. However, calculations suggest that this effect will not be dominant. These orientation effects should be most important for highly charged solutes for which chemical spin decoupling is not observed (Cr(III) experiment). Phosphorus decoupling is therefore not observed in a proton spectrum whose relaxation times are second sphere in nature, but proton decoupling should be observed in the phosphorus spectrum. If the relaxation times originate from a first-sphere interaction, chemical spin decoupling need not always occur.<sup>8</sup> For all compounds studied chemical spin decoupling is observed over the entire temperature range and the resulting relaxation times are first sphere in origin.

The phosphorus spin-lattice relaxation times may be obtained from the observed separation of the doublet as it coalesces into a single line. The following equation is

$$T_1 = P_M [2 / (1 - D^2) \pi^2 J^2]^{1/2}$$

applicable<sup>7,8</sup> where  $P_M$  is the probability of a ligand molecule being in the primary coordination sphere of the metal ion,  $D$  is the observed separation of peaks in the

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TABLE II  
 SUMMARY OF RELAXATION TIME DATA

Compound	Phosphorus		Protons		Temp range, °C
	1/T <sub>1</sub> , sec <sup>-1</sup>	-E <sub>A</sub> , kcal	1/T <sub>2</sub> , sec <sup>-1</sup>	-E <sub>A</sub> , kcal	
Mn(HMPA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	2.8 × 10 <sup>4</sup>	3.4	2.0 × 10 <sup>4</sup>	3-4	115-15 (Figure 3)
Fe(HMPA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	2.8 × 10 <sup>3</sup>	0.4	<i>b</i>		70-15
Co(HMPA) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub>	5.0 × 10 <sup>3</sup>	0.4	<i>b</i>		100-15
Mn(DMMP) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	8.7 × 10 <sup>3</sup>	4.0	1.1 × 10 <sup>4</sup> <sup>c</sup>	3.9 <sup>c</sup>	110-66
			1.7 × 10 <sup>4</sup> <sup>d</sup>	3.6 <sup>d</sup>	(Figure 2)
Mn(TMP) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	<i>a</i>		8.0 × 10 <sup>3</sup>	3.5	100-55

<sup>a</sup> The proton spin-spin relaxation time is sufficiently rapid as to make it difficult to obtain T<sub>1</sub> from the separation of the doublet over an extended temperature range. <sup>b</sup> Owing to solubility limits complete chemical spin decoupling cannot be achieved and proton transverse relaxation times cannot be readily obtained. <sup>c</sup> Methoxy proton data. <sup>d</sup> Methyl proton data.

presence of the paramagnetic metal divided by the coupling constant, *J*, in the absence of paramagnetic metal. At a sufficiently high concentration of paramagnetic metal chemical spin decoupling is complete and the line width, Δ*ν* (corrected for the natural line width in the absence of the complex), of the single remaining peak gives the proton transverse relaxation time (πΔ*ν* = P<sub>M</sub>/T<sub>2</sub>). This region is readily identified since Δ*ν* is a linear function of the concentration of the paramagnetic metal.<sup>7,8</sup>

A summary of the data at 25° is given in Table II. In all cases the small activation energies indicate that the exchange rates are greater than the relaxation rates. Therefore only limits can be set on the exchange rates, *k* > 1/T<sub>1</sub>, 1/T<sub>2</sub>. To our knowledge very little work has been reported on tetrahedral systems.<sup>12</sup> Rate limits should be evaluated at the lowest temperature reported; for example, Mn(DMMP)<sub>6</sub><sup>2+</sup> undergoes exchange at least five times faster than Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> would at -66° (based on known activation energies).<sup>13</sup>

To a good approximation, 1/T<sub>1</sub> and 1/T<sub>2</sub> of nuclei bonded to paramagnetic ions reduce to<sup>10</sup>

$$T_1^{-1} = \frac{4\mu^2\gamma_I^2\beta^2}{30r^6} \left[ 3\tau_c + \frac{7\tau_c}{1 + \omega_s^2\tau_c^2} \right] + \frac{2S(S+1)A^2}{3\hbar^2} \left[ \frac{\tau_c}{1 + \omega_s^2\tau_c^2} \right] \quad (1)$$

$$T_2^{-1} = \frac{4\mu^2\gamma_I^2\beta^2}{60r^6} \left[ 7\tau_c + \frac{13\tau_c}{1 + \omega_s^2\tau_c^2} \right] + \frac{S(S+1)A^2}{3\hbar^2} \left[ \tau_c + \frac{\tau_c}{1 + \omega_s^2\tau_c^2} \right] \quad (2)$$

where *I* and *S* refer to the nuclear and electron spins, ω is the Larmor precessional frequency, *A* is the hyperfine coupling constant, τ<sub>c</sub> and τ<sub>e</sub> are the correlation times for dipolar and contact interactions. The first term in the above equations is due to a dipole-dipole interaction while the latter term results from electron delocalization effects, contact mechanism. The correlation times are given by<sup>10</sup>

$$\tau_e^{-1} = \tau_h^{-1} + \tau_s^{-1}$$

$$\tau_c^{-1} = \tau_r^{-1} + \tau_s^{-1}$$

where τ<sub>h</sub> is the chemical exchange time, τ<sub>s</sub> is an electronic relaxation time, and τ<sub>r</sub> is the ion tumbling time.

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The activation energies for the phosphorus relaxation rates of the Fe<sup>2+</sup> and Co<sup>2+</sup> tetrahedral compounds of HMPA are comparable to those reported for octahedral compounds and are assigned to a correlation time which is controlled by an electron relaxation time.<sup>10,14-17</sup> A more detailed explanation of all of the phosphorus relaxation time data requires values for the phosphorus hyperfine coupling constant (which must be obtained from the <sup>31</sup>P spectrum) and a consideration of the relative importance of the dipole-dipole and contact mechanism.<sup>18</sup> Owing to solubility limits, complete chemical spin decoupling for Fe(HMPA)<sub>4</sub><sup>2+</sup> and Co(HMPA)<sub>4</sub><sup>2+</sup> cannot be achieved<sup>7,8</sup> and the proton transverse relaxation times cannot be readily obtained.

The data for Mn(DMMP)<sub>6</sub><sup>2+</sup> are summarized in Figure 2 and Table II. The small activation energies eliminate τ<sub>h</sub> as a likely correlation time. Since τ<sub>s</sub> is expected to be approximately 10<sup>-9</sup> sec,<sup>10</sup> ω<sub>s</sub><sup>2</sup>τ<sub>s</sub><sup>2</sup> ≫ 1. Consequently the term τ<sub>s</sub>(1 + ω<sub>s</sub><sup>2</sup>τ<sub>s</sub><sup>2</sup>)<sup>-1</sup> is very small and T<sub>1P</sub> must be entirely dipolar in nature.<sup>19</sup> If a metal-phosphorus distance of 2.5 Å is substituted into eq 1 and τ<sub>c</sub> is calculated at each temperature, the apparent bend for T<sub>1P</sub> in Figure 2 is reproduced with values of τ<sub>c</sub>(25°) = 1.2 × 10<sup>-11</sup> sec and E<sub>A</sub> = 4.0 kcal. The values of τ<sub>c</sub> and E<sub>A</sub> are comparable to those for Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and are typical for τ<sub>r</sub>. A metal-OCH<sub>3</sub> proton distance of *r* = 5.5 Å was estimated from the following bond distances: Mn—O, 1.4 Å; P=O, 1.5 Å; P—O, 1.6 Å; O—C, 1.4 Å; C—H, 1.1 Å; and from the bond angles: ∠MnO=P = 180°; ∠OPO = ∠POC = ∠OCH = 109°. If we now assume that T<sub>2H</sub> is also dipolar, T<sub>2H</sub>/T<sub>1P</sub> ≈ 8. This is not consistent with the near-equal ratio reported in Figure 2. The values of T<sub>2H</sub> are approximately an order of magnitude shorter than predicted by a dipolar mechanism. We therefore conclude that T<sub>2H</sub> is dominated by a contact interaction. The term τ<sub>s</sub> + [τ<sub>s</sub>/(1 + ω<sub>s</sub><sup>2</sup>τ<sub>s</sub><sup>2</sup>)] does not become small when ω<sub>s</sub><sup>2</sup>τ<sub>s</sub><sup>2</sup> ≫ 1. Because τ<sub>s</sub> is approximately two orders of magnitude longer than τ<sub>r</sub>, only a small contact shift (~200 cps) from which *A* is calculated<sup>20</sup> is sufficient to dominate the dipolar term. A contact shift of this magnitude is too small to be ac-

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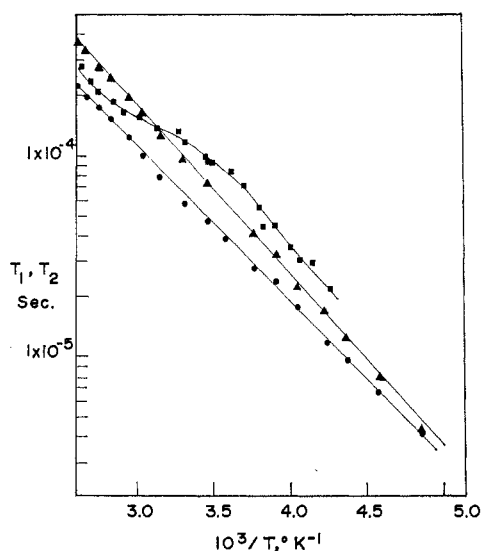


Figure 2.—The temperature dependence of the phosphorus relaxation time  $T_1$  (■) and the proton spin-spin relaxation time  $T_2$  of the methyl (●) and methoxy protons (▲) of  $\text{Mn}(\text{DMMP})_6^{2+}$ .

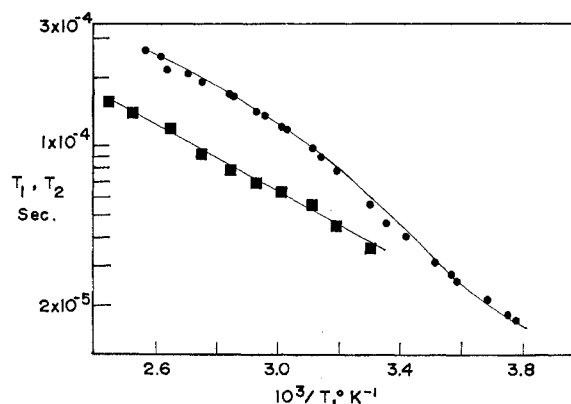


Figure 3.—The temperature dependence of the phosphorus relaxation time  $T_1$  (■) and the proton spin-spin relaxation time  $T_2$  (●) of  $\text{Mn}(\text{HMPA})_4^{2+}$ .

curately measured under rapid exchange conditions. The proton activation energies, Table II, are comparable to  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ .<sup>18</sup> The  $T_{2\text{H}}$  values show no nonlinearity because  $T_{2\text{H}}$  is largely due to a contact interaction with  $\tau_c = \tau_s$ . Considering the temperature range (110 to  $-66^\circ$ ) the values of  $T_{2\text{H}}$  give a surprisingly good fit to a simple exponential temperature dependence. The relative values of the proton relaxation times of the methyl and methoxy groups are consistent with coordination through the phosphoryl group.

The phosphorus relaxation times of  $\text{Mn}(\text{TMP})_6^{2+}$  cannot readily be obtained over an extended temperature range by measuring the separation of the doublet. The data for  $T_{2\text{H}}$  give a good fit to a simple exponential plot and are comparable to those of  $\text{Mn}(\text{DMMP})_6^{2+}$ , Table II.

The data for  $\text{Mn}(\text{HMPA})_4^{2+}$  are summarized in Figure 3. The relative values of  $T_{2\text{H}}$  and  $T_{1\text{P}}$  clearly show that a dipolar mechanism cannot be operative for both  $T_{2\text{H}}$  and  $T_{1\text{P}}$ . Since no reliable estimates have been

made for  $\tau_c$ , one cannot confidently conclude that  $T_{1\text{P}}$  is dipolar in nature. Since  $T_{2\text{H}}$  is too small relative to  $T_{1\text{P}}$ ,  $T_{2\text{H}}$  must contain an appreciable contribution from a contact interaction. The deviation from linearity for  $T_{2\text{H}}$  is probably due to small differences in the temperature dependence of  $\tau_c$  and  $\tau_s$ . The activation energies, Table II, are comparable to those of octahedral systems.

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## Pyrolysis of Disilane and Trisilane

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The preparation of polysilanes from monosilane by an electric discharge in a flow system has been reported by Spanier and MacDiarmid.<sup>1</sup> Fritz<sup>2</sup> has also demonstrated that polysilanes are produced during the pyrolysis of silane. In this note we report our results on the preparation of trisilane and tetrasilane by the flow system pyrolysis of disilane and trisilane, respectively.

Our results on the disilane pyrolysis have demonstrated that the primary decomposition does not produce hydrogen. Also, our data are not in accord with the decomposition of disilane into silyl radicals. Therefore, our results are most consistent with the decomposition of disilane into silane and silene followed by silene insertion into disilane forming trisilane.

### Experimental Section

These experiments were carried out in standard high-vacuum systems. Separations were made by trap to trap distillations. The reactants and products were identified by their infrared<sup>1,3-5</sup> and mass spectra (see Table I).

TABLE I

MASS SPECTRUM OF PRODUCTS				
$\text{SiH}_x^+$ m/e	$\text{Si}_2\text{H}_x^+$ m/e	$\text{Si}_3\text{H}_x^+$ m/e	$\text{Si}_4\text{H}_x^+$ m/e	$\text{Si}_5\text{H}_x^+$ m/e
28-34	56-64	84-96	112-126	140-156
$\text{Si}_2\text{H}_6$	81	248	0	0
$\text{Si}_3\text{H}_8$	18	146	83	0
$\text{Si}_4\text{H}_{10}$	22	84	199	57

Disilane was prepared by the reduction of hexachlorodisilane with lithium aluminum hydride. The trisilane used was obtained from the pyrolysis of disilane as described herein.

The pyrolysis reactions were carried out in a Pyrex tube with a diameter of 6 mm and an effective volume of 3.8 cm<sup>3</sup>. The reaction chamber was connected to an automatic Toepler pump for cycling. The inner walls were coated with a silicon mirror from previous pyrolysis reactions. Three runs were made over an uncoated surface by adding Pyrex beads to the reaction chamber.

The chamber was heated with a heating tape which surrounded a thermometer placed between the tape and the chamber. The heating tape was then wrapped with several layers of asbestos. The disilane pressure in the chamber was about 30 Torr which

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