benzene and chloroform solutions containing equimolar mixtures (*ca.* 4.4 mmoles/l. each) of the methyl and the ethyl derivative were stored for 1 hr at 25° in a closed system under nitrogen. Solvent was then removed from each solution in a stream of nitrogen and the residual solids were dried for 1 hr at 25° (~0.01 mm). Mass spectra of these samples showed only ions attributable to the parent methyl and ethyl complexes, and none due to mixed derivatives of the type $Mn_4(CO)_{12}(SCH_3)_n(SC_2H_5)_{4-n}$ ($n = 1$–3). The latter would be expected to form if equilibrium between the trimeric and the tetrameric species were indeed established in solution. Hence these results support retention of integrity of the tetramers in solution; the apparently contradictory evidence derived from the molecular weight data is not understood.

The exclusively tetrameric nature of $[Mn(CO)_3SR]_n$ species when contrasted with the prevalence of both $[Re(CO)_3SR]_3$ and $[Re(CO)_3SR]_4$[4] further emphasizes structural differences between compounds of the same apparent chemical composition formed by the first and third members of a transition metal triad.[13] Although the structures of $[Mn(CO)_3SR]_4$ cannot be elucidated from the data on hand, one possible molecular arrangement, which bears resemblance to that found in $[(CH_3)_3PtCl]_4$,[14] is depicted in Figure 1. Here each sulfur atom functions as a five-electron donor and no metal–metal bonding need be invoked. Alternatively, the SR groups could lie along four of the edges of a manganese tetrahedron. Such a structure, shown in Figure 2, would require metal–metal interactions; moreover, the possibility of valence tautomerism involving other, similar forms also must be considered.

Acknowledgments.—P. J. P. and A. W. wish to acknowledge support of this study by the National Science Foundation. We are also grateful to Dr. E. W. Abel for the information concerning the molecular weights discussed herein.

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[13] See, for example, C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966), and references therein.

[14] R. E. Rundle and J. H. Sturdivant, *ibid.*, **69**, 1561 (1947).

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Nuclear Magnetic Resonance Studies on Redistribution Reactions of Some Pentavalent Organoantimony and Organoarsenic Dihalides[1]

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Received May 8, 1967

As previously reported,[2] solutions of two different trimethylantimony dihalides, $(CH_3)_3SbX_2$ and $(CH_3)_3SbY_2$, disproportionate when mixed and form a mixed halide, $(CH_3)_3SbXY$. Similar redistribution reactions have now been observed with compounds in each of the following additional dihalide series: (a) trimethylarsenic, $(CH_3)_3AsX_2$; (b) triphenylarsenic, $(C_6H_5)_3AsX_2$; (c) tribenzylarsenic, $(C_6H_5CH_2)_3AsX_2$; (d) triphenylantimony, $(C_6H_5)_3SbX_2$; and (e) tribenzylantimony, $(C_6H_5CH_2)_3SbX_2$. Reported in this paper are pmr and ^{19}F chemical shifts for the various species in solution and equilibrium constants for redistribution reactions for each series.

Experimental Section

The ^1H and ^{19}F nmr studies were carried out using a Varian HA-100 high-resolution spectrometer equipped with a variable-temperature probe. The temperature of the sample was regulated to ±1° by a Varian variable-temperature controller (V4343) which had been previously calibrated with a thermocouple in place of the sample. The pmr spectra were run on precalibrated chart paper at either 500- or 250-cps sweep width with tetramethylsilane as the internal reference. The ^{19}F chemical shifts were obtained by the side-band technique with $CFCl_3$ as the internal reference. The concentrations of the samples studied ranged from 0.025 to 0.300 *M* in $CDCl_3$ or $CHCl_3$. The concentration chosen for a given series depended upon the solubility of the compounds. In Table I are reported the pmr and ^{19}F nmr spectral parameters for the various parent dihalides and mixed halides in $CHCl_3$ solution. The chemical shifts for the methyl and methylene protons given in Table I are essentially temperature independent from −20 to 70°.

TABLE I

METHYL AND METHYLENE PROTON AND ^{19}F CHEMICAL SHIFTS FOR R_3MX_2 AND R_3MXY SPECIES IN SOLUTION[a,b]

Species in $CHCl_3$ soln	δ,[c] ppm downfield from TMS at −60°	ϕ^*,[c] ppm upfield from $CFCl_3$ at −60°
$(CH_3)_3AsF_2$	2.17 (t)	53.2 (m)
$(CH_3)_3AsCl_2$	3.00 (s)	...
$(CH_3)_3AsFCl$	2.66 (d)	77.4 (m)
$(CH_3)_3AsBr_2$	3.23 (s)	...
$(C_6H_5CH_2)_3AsF_2$	3.25 (t)	76.0 (m)
$(C_6H_5CH_2)_3AsCl_2$	3.92 (s)	...
$(C_6H_5CH_2)_3AsFCl$	3.66 (d)	99.7 (m)
$(C_6H_5)_3AsF_2$	...	87.3
$(C_6H_5)_3AsFCl$	...	68.8
$(C_6H_5CH_2)_3SbF_2$	3.26 (t)	126.6 (m)
$(C_6H_5CH_2)_3SbCl_2$	3.72 (s)	...
$(C_6H_5CH_2)_3SbFCl$	3.46 (d)	131.7 (m)

[a] Chemical shift values for species in solution where R = CH_3 or C_6H_5, M = Sb, and X = F, Cl, Br, or I are given in ref 2. [b] Chemical shift values reported for the mixed halide species are for separate signals, *i.e.*, no exchange averaging. [c] t = triplet, d = doublet, s = singlet, m = multiplet.

At least ten independent measurements on each of a series of solutions over a range of relative concentrations of the reactants of 1:2 to 2:1 were made in arriving at the values of *K* reported in Table II. The ranges of values obtained are given in Table II.

The majority of the compounds studied were prepared by following known procedures.[3–7] Triphenylantimony dichloride was

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[1] Presented in part before the Division of Inorganic Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

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[3] G. G. Long, G. O. Doak, and L. D. Freedman, *J. Am. Chem. Soc.*, **86**, 209 (1964).

[4] G. O. Doak, G. G. Long, and L. D. Freedman, *J. Organometal. Chem.* (Amsterdam), **4**, 82 (1965).

[5] M. H. O'Brien, G. O. Doak, and G. G. Long, *Inorg. Chim. Acta*, **1**, 34 (1967).

[6] I. P. Tsukervanik and D. Smirnov, *Zh. Obshch. Khim.*, **7**, 1527 (1937); *Chem. Abstr.*, **31**, 8518 (1937).

[7] G. T. Morgan and F. M. G. Micklethwait, *Proc. Chem. Soc.*, **28**, 68 (1912).

TABLE II

EQUILIBRIUM CONSTANTS FOR REDISTRIBUTION REACTIONS OF TYPES 1–5

$$1.\quad (CH_3)_3SbX_2 + (CH_3)_3SbY_2 \rightleftharpoons 2(CH_3)_3SbXY$$

	X	Y	K 0°	K 35°	K 60°
(a)	F	Cl	. . .	3.90 ± 0.15	4.20 ± 0.10
(b)	F	Br	2.81 ± 0.09	3.24 ± 0.14	3.61 ± 0.19
(c)	F	I	1.09 ± 0.10	1.50 ± 0.06	1.68 ± 0.13
(d)	Cl	Br	3.28 ± 0.20	3.50 ± 0.15	3.65 ± 0.13
(e)	Cl	I	2.05 ± 0.07	2.25 ± 0.10	2.85 ± 0.08
(f)	Br	I	2.93 ± 0.03	3.02 ± 0.10	3.30 ± 0.16

$$2.\quad (C_6H_5)_3SbX_2 + (C_6H_5)_3SbF_2 \rightleftharpoons 2(C_6H_5)_3SbFX$$

	X	K (35°)
(a)	Cl	9.0 ± 1.2
(b)	Br	4.0 ± 0.7
(c)	I	1.0 ± 0.3

$$3.\quad (C_6H_5CH_2)_3SbF_2 + (C_6H_5CH_2)_3SbCl_2 \rightleftharpoons 2(C_6H_5CH_2)_3SbFCl$$
$$K = 6.4 \pm 0.5 \text{ at } -37°$$

$$4.\quad (CH_3)_3AsF_2 + (CH_3)_3AsCl_2 \rightleftharpoons 2(CH_3)_3AsFCl$$
$$K = 5.4 \pm 0.6 \text{ at } -53°$$

$$5.\quad (C_6H_5CH_2)_3AsF_2 + (C_6H_5CH_2)_3AsCl_2 \rightleftharpoons 2(C_6H_5CH_2)_3AsFCl$$
$$K = 10 \pm 1 \text{ at } -47°$$

purchased from Eastman Organic Chemicals (EKC 4430). Tribenzylarsenic dichloride, mp 143–144°, was prepared by essentially the same procedure as was used to synthesize tribenzylantimony dichloride.[6]

Anal. Calcd for $C_{24}H_{21}AsCl_2$: C, 60.17; H, 5.05. Found: C, 60.40; H, 5.16.

Tribenzylarsenic Difluoride and Tribenzylantimony Difluoride.—These compounds were prepared by treating solutions of the respective dichlorides in acetonitrile (0.02 mole/150 ml) with an excess of solid AgF (Ozark-Mahoning Co.). The slurry was stirred and maintained just below the boiling point for 20 hr. Portions of the AgF (total ~7.5 g) were added to the reaction mixture until a negative test was obtained for chloride when a drop of the reaction mixture was added to alcoholic silver nitrate solution and a positive test was obtained for silver ion when a drop of the reaction mixture was added to alcoholic LiCl solution. The hot slurry was filtered to remove solids (AgCl and excess AgF) and the filtrate was evaporated to dryness on a rotatory evaporator. The brown residue was extracted with a total of 250 ml of boiling petroleum ether (65–110°). This hot petroleum ether extract was filtered to yield a clear colorless solution. White colorless needles formed on cooling which were recrystallized from petroleum ether.

The yield of recrystallized tribenzylarsenic difluoride, mp 104°, was 3.1 g (40%). *Anal.* Calcd for $C_{24}H_{21}AsF_2$: C, 65.29; H, 5.48. Found: C, 65.49; H, 5.60.

The yield of recrystallized tribenzylantimony difluoride, mp 113–115°, was 3.7 g (43%). *Anal.* Calcd for $C_{24}H_{21}SbF_2$: C, 58.23; H, 4.85. Found: C, 58.55; H, 4.81.

Results and Discussion

In earlier work,[2] we reported that the pmr spectra of chloroform solutions containing any pair of the trimethylantimony dihalides at room temperature consist of three methyl signals which are characteristic of the two dihalides and a third signal which we identified as the mixed halide. Integration of these three signals allows one to evaluate the equilibrium constants for the various redistribution reactions. The equilibrium constants calculated are given in Table II and are of the form

$$K = [(CH_3)_3SbXY]^2/[(CH_3)_3SbX_2][(CH_3)_3SbY_2]$$

where X, Y = F, Cl, Br, I.

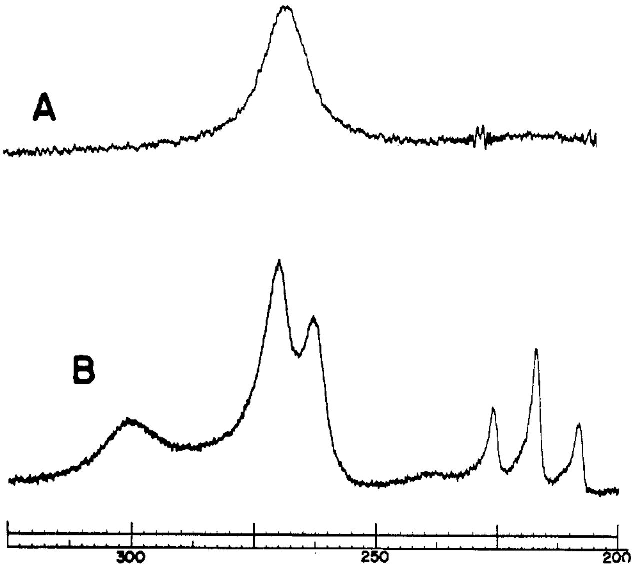

Figure 1.—Pmr spectra at 32° (A) and −60° (B) of $CHCl_3$ solutions of an equimolar mixture of $(CH_3)_3AsCl_2$ and $(CH_3)_3AsF_2$.

These data suggest that the equilibrium constants are approaching the statistical value of 4.0 as the difference in electronegativity between X and Y decreases and as the temperature increases. The deviations from statistical behavior are most likely attributable to nonzero values of the enthalpy. Using the value of K for reaction 1(c) at 35° (Table II), we find the deviation of the free energy for this reaction from the free energy corresponding to statistical behavior is equal to 0.60 kcal. As pointed out by Van Wazer,[8] this free energy deviation is essentially due to the enthalphy of the reaction. A plot of ln K for reaction 1(c) *vs.* $1/T$ gives $\Delta H = 1.3$ kcal. This relatively good agreement leads one to believe that the small deviations are real and that the measured equilibrium constants are reasonably accurate.

When solutions of two different trimethylarsenic dihalides are mixed at room temperature the pmr spectra show a single broad signal in the case of the difluoride–dichloride and the difluoride–dibromide solutions, but a sharp singlet in the case of the dichloride–dibromide solution. Upon cooling the difluoride–dichloride solution to −60°, three signals are observed (*cf.* Figure 1). Two of these signals correspond to the parent dichloride and difluoride; the third, a doublet, must be assigned to the fluoride–chloride species. Integration of these signals gives an equilibrium constant of 5.4 which is slightly greater than that observed for reaction 1(a) in Table II. In the case of the difluoride–dibromide and dichloride–dibromide solutions, the halide exchange is occurring too rapidly even at −60° to allow observation of the individual signals and calculation of equilibrium constants.

Redistribution reactions have also been observed when solutions of two different triphenylantimony dihalides are mixed at room temperature. In those cases where one is triphenylantimony difluoride, the

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[8] J. R. Van Wazer and K. Moedritzer, *Inorg. Chem.*, 3, 268 (1964).

formation of $(C_6H_5)_3SbFX$ is indicated by the appearance of ^{19}F signals $\sim$20 ppm to low field of the difluoride signal.[2] Comparison of the equilibrium constants for reactions 1(a)–(c) with 2(a)–(c), respectively, indicates that, in the case of the difluoride–dichloride reactions, the deviation from statistical behavior depends on the R group whereas in the cases of the difluoride–dibromide and difluoride–diiodide reactions, the different R groups do not significantly change the value of K. To date we have not been able to obtain reproducible values of equilibrium constants for reactions 2(a)–(c) at additional temperatures, because the ^{19}F signals saturate easily at higher temperatures and solubilities are reduced significantly at lower temperatures.

As shown in Table II, equilibrium constants have also been measured for the reactions between tribenzylarsenic difluoride and tribenzylarsenic dichloride (reaction 5) and for the analogous antimony compounds (reaction 3). A comparison of the equilibrium constants for these reactions with those of reactions 1(a), 2(a), and 4 is further evidence that the deviation from statistical behavior for the difluoride–dichloride reactions is a function of the R group. As shown in Table II the equilibrium constants increase in the manner $CH_3 < C_6H_5CH_2 < C_6H_5$ for reactions of types 1(a), 2(a), and 3. In the case of the analogous arsenic compound reactions, namely, 4 and 5, the equilibrium constant is also larger where R is benzyl.

Likewise, a comparison of reactions 3 with 5 and 1(a) with 4 indicates that the central atom has some effect on the equilibrium constants.

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Water Exchange with the Monoamminepentaaquonickel(II) Ion[1]

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Received November 9, 1967

We are concerned here with direct measurements of the effect of substitution on water lability in aquo ions. Previous ^{17}O nmr studies have been made on NCS^- and Cl^- effects, for example.[2,3] In these cases considerable uncertainty about species exists and it was felt that the ammine system of Ni(II) would be easier to interpret. Indirect studies on water lability have been made for some time.[4]

Experimental Section

The nmr techniques and the treatment of the data have been discussed previously.[2a] Signal enhancement was obtained here by using a Fabritek LSH1024 point signal averager.

Solutions were prepared using redistilled water containing 1.19 atom % ^{17}O (*ca.* 17% ^{18}O and normal H content) obtained from Bio-Rad Laboratories. Other reagents used were Mallinckrodt AR grade $Ni(NO_3)_2 \cdot 6H_2O$ and NH_4NO_3 and Baker Analyzed NaOH. The pH was measured to ±0.01 pH unit using a Beckman Research Model pH meter.

The values for the acid dissociation constant of NH_4^+ used were those given by Bates and Pinching.[5] Ionic strength corrections to the pH and ammine complex constant data used were those of Bjerrum.[6]

Results

The experimental data are given in Table I. The symbols have the following meanings:[2] Δ' is the line broadening, in gauss, produced by Ni(II) in $H_2{}^{17}O$, W_0 is the full line width at half-maximum absorption for the reference solution not containing Ni(II) (Δ' is $W_{obsd} - W_0$), and T'_{2p} is defined as $2M(Ni)_T/\gamma\Delta'$, where $M(Ni)_T$ refers to total nickel molarity and γ is the magnetogyric ratio for ^{17}O (3628 gauss^{-1} sec^{-1}).

As a check on the procedures the solution at pH 6.28 was acidified to *ca.* 0.5 M H^+ with HNO_3, and line broadenings at three temperatures were obtained in good agreement with those of Swift and Connick[7] indicating that no appreciable effects were caused by 2 M NH_4NO_3.

The temperature dependences of the line broadenings at the lower temperatures are consistent with control of broadening by the chemical-exchange rate.[7] In this case $T'_{2p} = M(Ni)_T\tau_L$ where τ_L is the mean life for exchange of a free water molecule with bound water molecules. The total rate of water exchange (M sec^{-1}) is $[H_2O]/\tau_L$ or $55.5/T'_{2p}$ for 1 M Ni(II). At 25° in 1 M Ni(II) solutions the total exchange rate for water in $Ni(H_2O)_6{}^{2+}$ solution[7] is 1.62×10^5 M sec^{-1} (*i.e.*, $6k_1$). In our solutions the comparable rates are: for pH 5.75, 4.11×10^5; pH 6.08, 4.63×10^5; and pH 6.38, 5.84×10^5. Thus labilization of water has occurred.

The ammonia concentration in these solutions is too low to permit nmr studies of the ammonia-exchange rate for comparison. Rorabacher[8] has measured the formation rate for the monoammine species using the temperature-jump–relaxation method and it is clear from his data that the process

$$Ni(H_2O)_6{}^{2+} + NH_3 \rightleftharpoons Ni(H_2O)_5NH_3{}^{2+} + H_2O$$

is much too slow to account for our results. The effect of pH alone on the $Ni(H_2O)_6{}^{2+}$ system seems not to have been studied. Hydrolysis of nickel aquo ion appears to be slight and it seems to us likely that the observed rate increase is due to formation of ammine complexes of greater lability than the aquo ion. The results can be approximately rationalized taking $R_{total} = R_{aquo} + R_{monoammine}$ and assuming that R_{aquo} has

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(1) Supported by USAEC Contract AT(45-1)-2040; Report RLO-2040-2.

(2 (a) R. B. Jordan, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **5**, 1906 (1966); (b) S. F. Lincoln, F. Aprile, H. W. Dodgen, and J. P. Hunt, submitted for publication.

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