CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA 55455, AND PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

Organometallic Condensation Reactions. The Hydrolysis of Dimethylgallium(III) and the Growth of Bis- and Tetrakis(dimethylgallium hydroxide)[1]

BY LORENZO PELLERITO[2] AND R. STUART TOBIAS[3]

Received October 16, 1969

The hydrolysis of the cation $(CH_3)_2Ga(OH_2)_2^+$ has been studied in a 0.3 *M* (Na)ClO$_4$ medium at 25° by potentiometric measurements using glass electrodes. The only hydrolysis products observed up to pH *ca.* 7 were the mononuclear species $(CH_3)_2GaOH$ and the dimer $[(CH_3)_2GaOH]_2$. The formation constants are $\log {}^*\beta_{11} = -5.45 \pm 0.01$ and $\log {}^*\beta_{22} = -8.33 \pm 0.01$. Consequently, the constant for the dimerization process $2(CH_3)_2GaOH = (CH_3)_2Ga(OH)_2Ga(CH_3)_2$ is $\log K_d = 2.57 \pm 0.02$. It is likely that the structure of the dimer is similar to that of $[(CH_3)_2GaCl]_2$ and to trimethylsiloxydimethylgallium(III) which is dimeric. The tetrameric hydroxide which is the solid product obtained by hydrolysis of $(CH_3)_3Ga \cdot O(C_2H_5)_2$ is not present in aqueous solution in significant concentrations.

Introduction

Recently, we have examined the hydrolysis of the square-planar organo(transition metal) cation *cis*-$(CH_3)_2Au(OH_2)_2^+$.[4] Although the main solid product isolated after reaction of $(CH_3)_2Au^{III}$ and OH^- in aqueous solution contains tetrameric $[(CH_3)_2AuOH]_4$[5] which crystallizes in the orthorhombic system (space group Pbca), no significant concentration of the tetrameric molecule is present in solution. Only the dimer $[(CH_3)_2AuOH]_2$ is a significant solute species.

The hydrolysis of the trimethylgallium diethyl etherate gives, upon isolation of the product from solution, tetrameric $[(CH_3)_2GaOH]_4$.[6,7] This compound crystallizes in the monoclinic system (space group $P2_1/c$).[8] The structures of these two hydroxides $[(CH_3)_2AuOH]_4$ and $[(CH_3)_2GaOH]_4$ have been discussed in a recent paper.[9]

The cation $(CH_3)_2Ga(OH_2)_2^+$ is stable in aqueous solution and has essentially a tetrahedral structure.[9] Although water molecules bound in the first coordination sphere of Ga^{3+} exchange rather slowly (on the ^{17}O nmr scale) with the bulk solvent water,[9-11] water molecules bound to $(CH_3)_2Ga^+$ exchange much more rapidly[12] because of the very polarizable methyl groups in the first coordination sphere of Ga(III). The methyl groups also lead to a decrease in the coordination number of Ga(III) from 6 to 4 in the dimethyl derivatives.

Experimental Section

Solutions.—Dimethylgallium(III) perchlorate solutions were prepared by dissolving weighed quantities of $[(CH_3)_2GaOH]_4$[7,13] in a known excess of dilute standard perchloric acid at 0°. Sodium perchlorate was prepared by reaction of Baker "Analyzed Reagent" Na_2CO_3 and a slight excess of $HClO_4$. Neutrality of the final product was ensured by titration of the excess acid with standard sodium hydroxide potentiometrically. The stock solution was analyzed by evaporation to constant weight. Perchloric acid solutions were prepared by dilution of Baker reagent 70–72% $HClO_4$ and were standardized against $KHCO_3$ and also against standard NaOH solutions. Carbonate-free NaOH solutions were prepared by dilution of a saturated solution with carbonate-free doubly distilled water and were standardized against potassium hydrogen phthalate.

Potentiometric Measurements.—The emf measurements were made using the Leeds and Northrup K-3 potentiometer–Cary 31V vibrating-reed electrometer circuit used in other work from this laboratory.[4,14] Beckman General Purpose electrodes were calibrated as hydrogen ion concentration probes in a 0.3 *M* $NaClO_4$ ionic medium. This medium rather than 3 *M* $NaClO_4$ was employed because of the rather low solubility of the hydrolysis products of $(CH_3)_2Ga^{III}$. Cell 1 thermostated at 25°

$$\text{Ag, AgCl}\left|\begin{array}{l}[Cl^-] = 10\ \text{m}M\\ [Na^+] = 300\ \text{m}M\\ [ClO_4^-] = 290\ \text{m}M\end{array}\right\|\ 300\ \text{m}M\ NaClO_4$$

$$\left\|\begin{array}{l}[(CH_3)_2Ga^{III}] = B\ \text{m}M\\ [H^+]\\ [Na^+] = (300 - [H^+] - B)\ \text{m}M\\ [ClO_4^-] = 300\ \text{m}M\end{array}\right|\ \begin{array}{l}\text{glass}\\ \text{electrode}\end{array} \qquad (1)$$

was used for the measurements. Titrations were carried out by adding to acidic solutions of *B* m*M* $(CH_3)_2Ga^+$ equal volumes of NaOH solution and of an acidic solution of 2*B* m*M* $(CH_3)_2Ga^+$ in order to maintain the dimethylgallium(III) concentration constant. The values of *B* range from 3 to 22 m*M*.

The potentials, E_i, obtained in the first part of the titration of an acidic solution of $(CH_3)_2Ga^+$ where the analytical hydrogen ion concentration, *H*, can be taken as equal to the equilibrium hydrogen ion concentration, $[H^+]$, were fitted by least squares using the program NBAR[4] to the relation $E = E° + 59.15 \log [H^+] + k[H^+]$ to determine the best values of the parameters $E°$ and *k*. The experimental values of *k* were negative and in the range 0.10–0.25 mV/m*M*. These data were then used to determine the values of $[H^+]$ at pH values where the aquo cation begins to dissociate. The output from the NBAR program is $\bar{n}_i = ([H^+]_i - H_i)/B_i$, $\log [H^+]_i$, B_i, and $\sigma\bar{n}_i$. The errors in $\bar{n}$, $\sigma\bar{n}_i$, are calculated on the basis of the estimated errors in the analytical concentrations, the volume measurements, and the potentials E_i using the law for the propagation of variance.

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[1] Research supported by the National Science Foundation, Grants GP-7899 and GP-15083.

[2] Italian National Research Council (CNR) Fellow from the University of Palermo, Palermo, Italy.

[3] Department of Chemistry, Purdue University.

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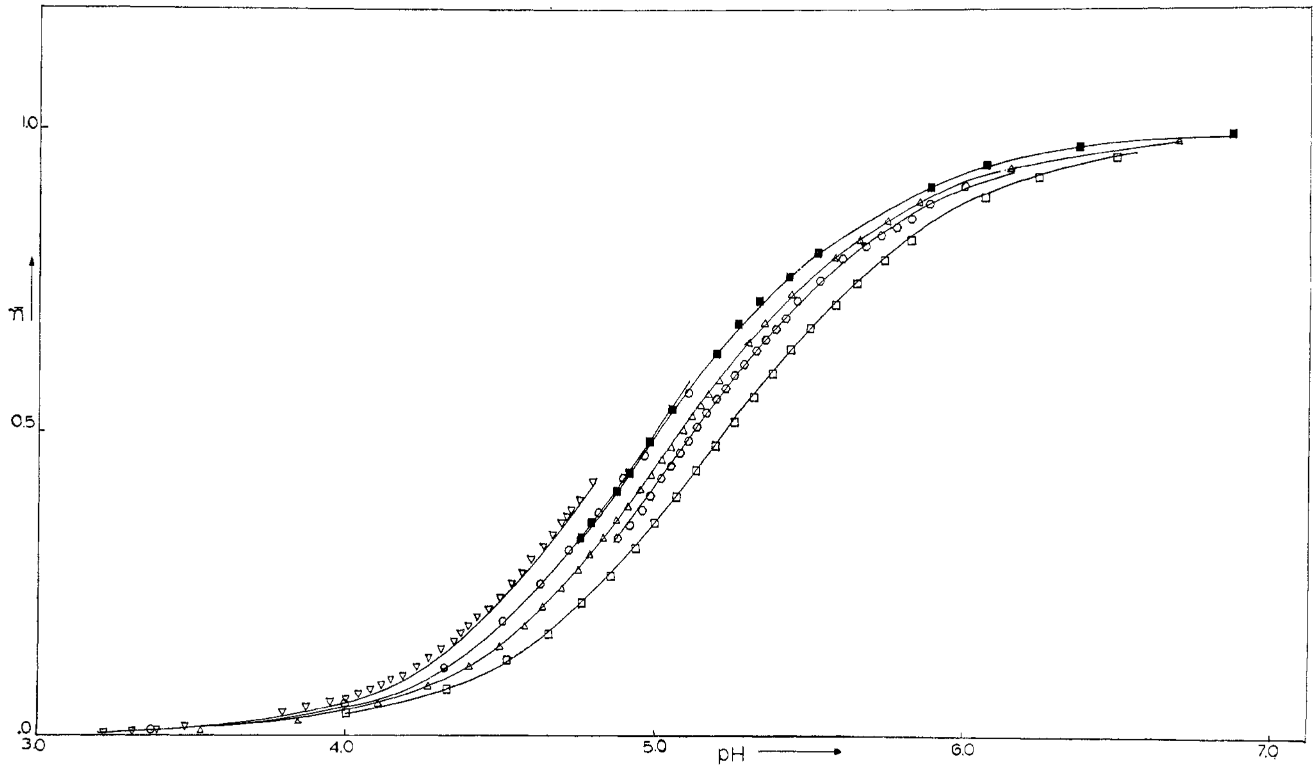

Figure 1.—Average number of protons transferred per $(CH_3)_2Ga^{III}$ as a function of $-\log [H^+]$. The solid lines are drawn using log $^*\beta_{11} = -5.45$, log $^*\beta_{22} = -8.33$. Millimolar concentration of $(CH_3)_2Ga^{III}$: □, 3.226; ⬡, 6.391; △, 8.391; ■, 13.26; ○, 14.03; ▽, 22.57.

Determination and Refinement of the Equilibrium Constants

The data $\bar{n}(\log [H^+])_B$, Figure 1, describe a family of curves indicating that polycondensed species are produced by the hydrolysis. A plot of log B *vs.* $(\log [H^+])_{\bar{n}}$ gives a family of approximately straight lines with slope *ca.* −2, and the $\bar{n}$ data can be normalized by replotting as a function of $\log B - 2 \log [H^+]$.[15] This suggests that the principal product of the hydrolysis is of the general type $[(CH_3)_2Ga]^+[(CH_3)_2Ga(OH)_2]^-_n$. Since $\bar{n}$ ranges only from 0 to 1.0, the 2:2 binuclear complex, $\bar{n} = 1$, is strongly indicated to be the principal hydrolysis product. A trial value of the equilibrium constant $^*\beta_{22}$[16] was obtained by plotting $\log (\bar{n}/4(1 - \bar{n})^2)$ *vs.* $\log B[H^+]^{-2}$. The data fall on a straight line of almost unit slope and with intercept $(\log {}^*\beta_{22} - \log 2)$.[17]

Since minor deviations between the observed points and those calculated assuming only the 2:2 complex suggested the presence of the 1:1 complex, a value of $^*\beta_{11}$ was estimated by plotting the quantity $\bar{n}[H^+]/B(1 - \bar{n})$ *vs.* $2B(1 - \bar{n})[H^+]^{-1}$ which gives a straight line of slope $^*\beta_{22}$ and intercept $^*\beta_{11}$.

In order to test other species, values for the equilibrium constants for the 3:3 and 4:4 complexes were estimated from approximate solutions to the simultaneous equations

$$[H^+]^{n}_{\bar{n}=0.5} = n{}^*\beta_{nn}[(CH_3)_2Ga^+]^{n-1} \qquad (2)$$

$$B = [(CH_3)_2Ga^+] + n{}^*\beta_{nn}[(CH_3)_2Ga^+]^n[H^+]^{-n}_{\bar{n}=0.5} \qquad (3)$$

The trial values for the constants were adjusted to minimize the sum of the squares of the weighted residuals in $\bar{n}$.[4] Weights, w_i, were set equal to $1/\sigma\bar{n}_i^2$. The results are collected in Table I together with the values of $s^2 = \Sigma_i w_i(\bar{n}_{i,\text{obsd}} - \bar{n}_{i,\text{calcd}})^2/(N_o - N_v)$. Here N_o is the number of data sets, 240, and N_v is the number of parameters being adjusted. Since s^2 gives an unbiased estimate of the variance and since

Table I

Results of the Least-Squares Refinements for Different Postulated Hydrolysis Products

Complex compn (metal atoms, protons transferred)	Log (equilibrium constants)[a]	$\frac{\Sigma_i w_i(\bar{n}_{i,\text{obsd}} - \bar{n}_{i,\text{calcd}})^2}{(N_o - N_v)}$
(1:1)	−5.07 ± 0.006	46.9
(2:2)	−8.08 ± 0.005	14.7
(3:3)	−10.95 ± 0.01	64.5
(4:4)	−13.76 ± 0.02	112.5
(1:1) + (2:2)	−5.45 ± 0.01, −8.33 ± 0.01	3.7
(2:2) + (1:2)	−8.08 ± 0.005, −13.7 ± 0.1[b]	14.7
(1:1) + (2:2) + (1:2)	−5.54 ± 0.01, −8.33 ± 0.01, 15.7 ± 5[b]	3.7
(1:1) + (2:2) + (3:3)	−5.45 ± 0.01, −8.33 ± 0.01, −13.9 ± 0.2[c]	3.7

[a] Valid at 25° in a 0.3 *M* ClO_4^- ionic medium. Standard errors are listed. [b] Does not converge; log $^*\beta_{12} \rightarrow -\infty$. [c] Does not converge; log $^*\beta_{33} \rightarrow -\infty$.

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(15) These procedures are discussed by F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., Chapter 17.

(16) The nomenclature for the equilibrium constants employed throughout is that of the Chemical Society tables, L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

(17) F. J. C. Rossotti and H. Rossotti, ref 15, p 366.

TABLE II

CALCULATED AND OBSERVED $\bar{n}$ VALUES AND THE ESTIMATED STANDARD ERRORS IN $\bar{n}$[a]

MCONC	-LOG H	NOBS	NCAL	SIGN
3.226	4.002	.044	.037	.017
3.226	4.313	.079	.077	.017
3.226	4.520	.123	.127	.017
3.226	4.663	.168	.176	.018
3.226	4.772	.214	.224	.018
3.226	4.862	.260	.271	.018
3.226	4.936	.305	.314	.018
3.226	5.007	.348	.358	.018
3.226	5.077	.391	.404	.018
3.226	5.140	.433	.446	.018
3.226	5.203	.475	.489	.018
3.226	5.263	.516	.529	.019
3.226	5.321	.556	.567	.019
3.226	5.377	.595	.603	.019
3.226	5.438	.633	.640	.019
3.226	5.505	.674	.679	.019
3.226	5.584	.708	.721	.019
3.226	5.656	.744	.756	.019
3.226	5.738	.779	.792	.019
3.226	5.830	.814	.827	.019
3.226	5.653	.849	.755	.020
3.226	6.071	.882	.895	.020
3.226	6.244	.915	.928	.020
3.226	6.491	.947	.958	.020
6.391	4.877	.320	.330	.008
6.391	4.919	.346	.358	.008
6.391	4.956	.370	.382	.008
6.391	4.986	.395	.403	.008
6.391	5.018	.418	.426	.008
6.391	5.052	.441	.449	.008
6.391	5.081	.464	.470	.009
6.391	5.111	.486	.490	.009
6.391	5.142	.508	.512	.009
6.391	5.174	.530	.534	.009
6.391	5.204	.550	.555	.009
6.391	5.233	.571	.574	.009
6.391	5.263	.591	.593	.009
6.391	5.295	.611	.614	.009
6.391	5.328	.630	.635	.009
6.391	5.358	.649	.653	.009
6.391	5.390	.667	.672	.009
6.391	5.423	.686	.691	.009
6.391	5.459	.721	.710	.009
6.391	5.530	.755	.746	.010
6.391	5.603	.788	.779	.010
6.391	5.685	.804	.813	.010
6.391	5.734	.819	.830	.010
6.391	5.778	.835	.845	.010
6.391	5.831	.850	.861	.010
6.391	5.886	.879	.876	.010
6.391	6.007	.908	.905	.010
6.391	4.874	.320	.328	.008
6.391	4.917	.346	.356	.008
6.391	4.954	.370	.381	.008
6.391	4.984	.395	.402	.008
6.391	5.019	.418	.426	.008
6.391	5.051	.442	.446	.008
6.391	5.080	.464	.469	.009
6.391	5.110	.486	.490	.009
6.391	5.142	.508	.512	.009
6.391	5.173	.530	.534	.009
6.391	5.204	.550	.555	.009
6.391	5.232	.571	.573	.009
6.391	5.262	.591	.593	.009
6.391	5.294	.611	.613	.009
6.391	5.327	.630	.634	.009
6.391	5.357	.649	.653	.009
6.391	5.389	.667	.671	.009
6.391	5.422	.686	.690	.009
6.391	5.457	.721	.709	.009
6.391	5.529	.755	.745	.010
6.391	5.601	.788	.779	.010
6.391	5.684	.804	.812	.010
6.391	5.732	.819	.830	.010
6.391	5.779	.835	.845	.010
6.391	5.830	.850	.861	.010
6.391	5.885	.879	.876	.010
6.391	5.999	.908	.903	.010
8.400	3.537	.002	.013	.003
8.400	3.855	.021	.026	.003
8.400	4.112	.050	.055	.003
8.400	4.274	.092	.084	.003
8.400	4.401	.114	.117	.003
8.400	4.503	.146	.152	.003
8.400	4.580	.177	.184	.003
8.400	4.644	.208	.215	.003
8.399	4.700	.238	.245	.003
8.400	4.749	.267	.273	.003
8.400	4.793	.295	.301	.003
8.400	4.835	.322	.328	.003
8.400	4.876	.349	.355	.003
8.400	4.916	.375	.382	.003
8.400	4.954	.400	.409	.003
8.400	4.991	.425	.435	.003
8.400	5.024	.449	.458	.003
8.400	5.055	.473	.481	.003
8.400	5.087	.496	.503	.003
8.400	5.117	.518	.524	.003
8.400	5.146	.540	.544	.003
8.400	5.162	.562	.555	.003
8.400	5.212	.582	.589	.003
8.400	5.305	.642	.648	.003
8.399	5.355	.680	.677	.003
8.400	5.438	.716	.723	.003
8.400	5.507	.751	.757	.004
8.399	5.581	.784	.790	.004
8.400	5.661	.815	.821	.004
8.399	5.752	.846	.851	.004
8.400	5.858	.875	.881	.004
8.400	6.148	.930	.937	.004
8.399	6.598	.982	.982	.004
13.065	3.926	.025	.037	.005
13.066	4.048	.064	.051	.005
13.066	4.299	.101	.099	.005
13.066	4.496	.177	.173	.005
13.066	4.569	.214	.208	.005
13.066	4.634	.250	.244	.005
13.065	4.702	.286	.265	.005
13.067	4.812	.354	.358	.005
13.066	4.911	.421	.429	.005
13.065	4.996	.464	.490	.005
13.066	5.083	.545	.552	.005
13.066	5.261	.659	.666	.005
13.066	5.463	.765	.772	.006
13.065	5.751	.864	.874	.006
13.065	6.159	.955	.948	.006
13.262	4.753	.325	.320	.004
13.262	4.796	.354	.349	.004
13.262	4.876	.409	.406	.004
13.262	4.914	.436	.432	.004
13.262	4.983	.488	.483	.004
13.262	5.056	.538	.535	.004
13.262	5.129	.585	.584	.004
13.262	5.201	.631	.632	.005
13.262	5.273	.674	.675	.005
13.262	5.394	.716	.740	.005
13.262	5.434	.755	.760	.005
13.262	5.525	.794	.799	.005
13.262	5.622	.831	.835	.005
13.262	5.743	.867	.872	.005
13.262	5.890	.901	.907	.005
13.262	6.081	.934	.939	.005
13.262	6.375	.965	.968	.005
13.262	6.872	.996	.990	.005
13.262	4.746	.325	.315	.004
13.262	4.790	.354	.344	.004
13.262	4.870	.409	.401	.004
13.262	4.907	.436	.428	.004
13.262	4.978	.488	.479	.004
13.262	5.051	.539	.531	.004
13.262	5.121	.585	.580	.004
13.262	5.196	.631	.629	.005
13.262	5.267	.674	.672	.005
13.262	5.344	.716	.715	.005
13.262	5.429	.754	.757	.005
13.262	5.521	.794	.797	.005
13.262	5.886	.901	.906	.005
13.262	6.075	.934	.938	.005
13.262	6.370	.966	.958	.005
13.262	6.864	.996	.990	.005
14.029	3.772	.007	.009	.006
14.029	3.998	.058	.045	.006
14.029	4.322	.123	.111	.006
14.029	4.515	.188	.187	.006
14.029	4.633	.250	.250	.006
14.029	4.720	.308	.304	.007
14.029	4.823	.364	.374	.007
14.029	4.901	.416	.430	.007
14.029	4.973	.466	.482	.007
14.029	5.112	.559	.580	.007
22.574	3.198	.004	.006	.006
22.576	3.287	.009	.007	.005
22.575	3.378	.014	.009	.006
22.575	3.418	.022	.011	.006
22.574	3.564	.026	.015	.006
22.575	3.647	.033	.019	.006
22.573	3.714	.040	.023	.006
22.575	3.791	.047	.029	.006
22.574	3.849	.055	.034	.006
22.574	3.931	.062	.043	.006
22.574	3.987	.070	.050	.006
22.575	4.021	.077	.056	.006
22.575	4.063	.085	.063	.006
22.574	4.100	.092	.070	.006
22.574	4.136	.093	.078	.006
22.575	4.169	.107	.086	.006
22.574	4.218	.122	.099	.006
22.575	4.254	.136	.110	.007
22.575	4.298	.149	.125	.007
22.574	4.331	.162	.137	.007
22.574	4.357	.175	.148	.007
22.574	4.386	.188	.160	.007
22.573	4.416	.200	.174	.007
22.574	4.440	.212	.185	.007
22.574	4.490	.234	.211	.007
22.574	4.525	.255	.231	.007
22.573	4.556	.276	.249	.007
22.573	4.590	.295	.271	.007
22.574	4.622	.313	.291	.007
22.574	4.648	.331	.309	.007
22.571	4.686	.355	.334	.007
22.573	4.704	.363	.347	.007
22.573	4.715	.378	.355	.007
22.573	4.737	.392	.370	.007
22.573	4.779	.419	.401	.008
22.574	3.215	.003	.006	.006
22.576	3.299	.008	.008	.006
22.575	3.394	.013	.010	.006
22.575	3.486	.019	.013	.006
22.574	3.580	.025	.016	.006
22.575	3.665	.032	.020	.006
22.573	3.731	.040	.024	.006
22.575	3.808	.047	.030	.006
22.574	3.866	.055	.035	.006
22.574	3.947	.062	.045	.006
22.574	4.004	.070	.053	.006
22.575	4.038	.077	.058	.006
22.575	4.080	.085	.066	.006
22.574	4.116	.092	.074	.006
22.574	4.153	.100	.082	.006
22.575	4.186	.107	.090	.006
22.574	4.235	.122	.104	.006
22.575	4.271	.136	.116	.007
22.575	4.315	.149	.131	.007
22.574	4.349	.162	.144	.007
22.574	4.375	.175	.155	.007
22.574	4.404	.188	.168	.007
22.573	4.433	.200	.182	.007
22.574	4.458	.212	.194	.007
22.574	4.507	.234	.220	.007
22.574	4.543	.255	.241	.007
22.573	4.573	.276	.259	.007
22.571	4.607	.295	.281	.007
22.574	4.639	.313	.302	.007
22.574	4.655	.331	.320	.007
22.571	4.702	.355	.346	.007
22.573	4.721	.363	.359	.007
22.573	4.732	.378	.367	.007
22.573	4.754	.392	.383	.007
22.573	4.796	.419	.413	.008

[a] All dimethylgallium(III) concentrations are in millimolar units.

weights were taken at $1/\sigma\bar{n}_i^2$, s^2 should be approximately unity if the proper constants have been obtained. The large value $s^2 = 46.9$ assuming only the 1:1 mononuclear complex is to be expected. The refinements with equilibrium constants for the 3:3 and 4:4 complexes gave even worse fits, $s^2 = 64.5$ and 112.5, respectively. The model involving both the 1:1 mononuclear and the 2:2 polynuclear complexes gives the best fit to the data. The incorporation of additional species gives no improvement in the fit and only insignificantly small values for the other equilibrium constants. Consequently the data indicate only the formation of the 1:1 and 2:2 species in the solutions. The output from the last least-squares cycle is collected in Table II. The distribution of $(CH_3)_2Ga^{III}$ among the different complexes for pH *ca.* 3–7 is illustrated in Figure 2.

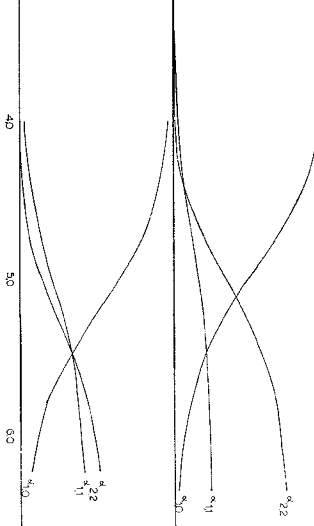

Figure 2.—Fraction of the $(CH_3)_2$GaIII present as different species α_{qp} (q is the number of $(CH_3)_2$GaIII; p is the number of protons transferred): top, total $[(CH_3)_2Ga^{III}]$ = 14.0 mM; bottom, total $[(CH_3)_2Ga^{III}]$ = 3.2 mM.

Discussion

The aquo cation is a weak acid, and one proton is transferred per dimethylgallium(III) in the pH range 4–6. Equilibria are rapid and reversible and attained within the time of mixing of the reagents. The dimethylgallium(III) ion is a slightly stronger acid than $(CH_3)_2Au^{III}$,[4] $\log {}^*\beta_{22} = -9.79 \pm 0.003$, but slightly weaker than CH_3Hg^+, $\log {}^*K_{11} = -4.59$.[18] It is interesting that the acidity does not correlate with the "covalency" of the metal–oxygen bonds as indicated by the intensity of Raman spectra, but it does correlate with the bond strengths measured by the metal–oxygen stretching frequencies. The dimethylgold ion gives a well-resolved Raman line due to Au–O bond stretching at 418 cm^{-1} with perchlorate solutions which shifts to 441 cm^{-1} for the dimethylgold(III) anion present in strongly alkaline solutions. The corresponding Ga–O stretch is too low in intensity to be recorded for the cation, although it appears weakly with the anion in alkaline solution at 495 cm^{-1}. Thus $(CH_3)_2Ga^{III}$ perturbs the bound water molecules somewhat more than $(CH_3)_2Au^{III}$ and the Ga–O bond is stronger than the Au–O bond, although the bond stretching vibration appears to cause a greater change in the molecular polarizability in the latter case, probably because of the participation of the penultimate d orbitals in the bonding.

Although the solid hydroxides isolated from the hydrolysis of dimethylgallium(III) and dimethylgold(III) contain tetrameric molecules, at least in the crystalline forms which have been examined by X-ray diffraction,[5,8] dimers are the predominant structures in both

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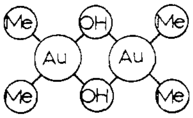
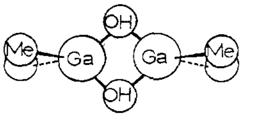
[18] G. Schwarzenbach and M. Schellenberg, *Helv. Chim. Acta*, **48**, 28 (1965).

solutions. The equilibrium constant for the dimerization process $2(CH_3)_2Ga(OH)(OH_2) = (CH_3)_2Ga(OH)_2Ga(CH_3)_2 + 2H_2O$ is $\log K_d = \log ({*\beta_{22}}/{*\beta_{11}}^2) = 2.57 \pm 0.02$. This value is rather typical for such dimerization processes which generally have equilibrium constants of *ca.* 10^3 and which appear to be relatively insensitive to the charge on the dimerizing species. The corresponding value for $2(CH_3)_2SnOH^+(aq) = (CH_3)_2Sn(OH)_2Sn(CH_3)_2^{2+}(aq)$ is $\log K_d = 2.48 \pm 0.02$.[14,19]

The high stability of these binuclear (2:2) dimethylgold and -gallium(III) complexes in solution is surprising. If they have the di-μ-hydroxo-bridged structures I and II, normal metal–oxygen bond lengths would lead to short metal–metal distances. Indeed, it is on this basis that the formation of the tetrameric hydroxides observed in the solid state is rationalized. Dimethylgallium chloride, bromide, and iodide are all dimeric molecules,[20] while the fluoride has been found in tri-[21] and tetrameric forms.[22]



(I)



(II)

Oxygen-bridged species with structures analogous to that suggested for the dimeric hydroxide have been proposed for both trimethylsiloxydimethylgallium(III)[23] and trimethylsiloxydimethylgold(III)[24] which are dimeric in organic solvents. In the case of trimethylsiloxydimethylaluminum(III), the presence of the four-membered ring has been verified by an X-ray structure determination.[25] With dimethylgallium hydroxide, it appears that the enthalpy change for polymerization–depolymerization is small, so that the particular molecular form isolated in the solid will be influenced by packing considerations in the crystal. The absence in aqueous solution of larger polymers such as the tetramers is not surprising, for their solubility should be very low.

The particular stability of the uncharged hydroxo complex is emphasized in both the $(CH_3)_2Ga^{III}$ and $(CH_3)_2Au^{III}$ cases by the fact that the $\bar{n}(\log [H^+])$ curves approach $\bar{n} = 1$ asymptotically. Only at much higher pH values will the solid hydroxides $[(CH_3)_2AuOH]_4$ and $[(CH_3)_2GaOH]_4$ dissolve to give anionic species.

Coordination of two methyl groups to Ga(III) has several important effects. First, it is likely that the coordination number for gallium changes from the value of 6 which is known to be the hydration number of Ga^{3+} to 4 (two CH_3, two H_2O). Second, the rate of exchange of bound and bulk water is greatly increased by the presence of the two methyl groups. Finally, the acidity is greatly reduced. Solutions of Ga^{3+} are highly hydrolyzed and equilibria are attained only very slowly.[26]

Acknowledgment.—We wish to express our appreciation to the Italian National Research Council (CNR) for a fellowship awarded to L. P.

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Notes

Contribution from the Department of Chemistry,
Louisiana State University in New Orleans,
New Orleans, Louisiana 70122

Structural and Spectroscopic Characteristics of the Nonachlorodirhodate(III) Anion

By R. A. Work, III, and M. L. Good

Received July 8, 1969

During a general investigation of the extraction of the group VIII metals as anionic complexes by long-chain quaternary ammonium compounds,[1] the extraction of rhodium(III) from an aqueous chloride solution was attempted. Since excess chloride ion was present, the anticipated extracted species was hexachlororhodate(III); however the observed visible spectrum was unlike that reported for this species or any other octahedral aquochloro complex reported by Kleinberg and coworkers.[2] In an attempt to identify the extracted species, several solid, short-chain quaternary ammonium chloride–rhodium(III) chloride compounds were prepared. The subsequent investigation yielded the results reported here.

Experimental Section

Extraction.—Aqueous solutions of either sodium hexachlororhodate(III) or rhodium trichloride trihydrate were extracted with a benzene solution of "Aliquat-336."[3] The organic layer was separated and dried for at least 24 hr over silica gel. Varying concentrations of all reagents mentioned above were used

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(1) M. L. Good and S. C. Srivastava, *J. Inorg. Nucl. Chem.*, **27**, 2429 (1965), and references cited therein.

(2) W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, **2**, 463 (1963).

(3) "Aliquat-336," subsequently referred to as A-336, is a mixture of long-chain, C_8–C_{10}, substituted quaternary ammonium chlorides consisting mainly of tricaprylylmonomethylammonium chloride obtained from General Mills.