large pseudocontact shift contribution in the six-coordinate cobalt(II)–histidine complexes. In this case, the observed $\Delta\Delta\nu$ differences do not necessarily reflect a different metal ion–ligand interaction, *i.e.*, Fermi contact difference.

Our results are in agreement with those reported by Holm, *et al.*,[6c] for the nickel(II)-substituted bis(β-ketoamines), except when a $C_6H_5C_2H_5$ group is substituted. Since the *meso*-$Ni(C_6H_5C_2H_5{-}C_6H_5HCH_3)_2$ complex exhibits anomalous behavior at low temperatures, which suggest hindered rotation about the N–C bond, it is probable that such steric factors enhance $\Delta\Delta\nu$ in this complex. If our results for "octahedral" nickel(II) systems can be extrapolated to tetrahedral nickel(II) systems, then our results support Holm's proposal[6c] that the large differences in the contact shifts of diastereoisomeric nickel(II) complexes that undergo planar $\leftrightarrow$ tetrahedral equilibrium are due chiefly to difference in the free energy, $\Delta\Delta G$. They are also in agreement with the relatively small differences in $\Delta\Delta\nu$, recently reported by Pignolet and Horrocks[8] for the pseudotetrahedral dihalogenobis(phosphine) complexes of nickel(II) and cobalt(II). However, rigorous interpretation of these data[8] is clouded by the fact that appreciable pseudocontact shift contributions may also be present in "tetrahedral" nickel(II) systems.[35]

Recently Holm and coworkers[6d] reported nonidentical resonances for the diastereoisomers $\Delta(+,+)$, $\Lambda(-,-)$ and $\Delta(-,-)$, $\Lambda(+,+)$ of pseudotetrahedral complexes possessing a large activation energy for racemization. However, in agreement with an earlier report,[6c] we were unable to detect a separate nmr resonance for different absolute configurations Λ(d,d,d) and Δ(d,d,d). This may be due to rapid racemization—the lifetime has been recently estimated[6c] to be 10^{-3} sec—or small differences in the shifts which are obscured by the broad, ill-resolved peaks.

In conclusion, our results show that chemical shift differences between diastereoisomers are enhanced either not at all or at most within the error limits of our measurement by a Fermi contact interaction. This enhancement is not as large as in previously reported cases[7] where other factors may contribute to the observed chemical shift difference. In view of the sensitivity of the contact shift experiment, it appears that in the complexes studied here there is at most a very slight difference in the metal–ligand interaction of the diastereoisomers. In diamagnetic complexes neighbor anisotropies are probably more significant in accounting for differences in many of the systems studied.

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Inorganic Condensation Reactions. The Hydrolysis of Dimethylgold(III) and the Growth of Tetrakis(dimethylgold hydroxide)[1]

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The hydrolysis of the cation $(CH_3)_2Au(OH_2)_2^+$ has been studied in a 0.3 *M* (Na)ClO$_4$ medium at 25° by potentiometric measurements using glass electrodes. The only significant species aside from the aquo ion up to pH *ca.* 8 is the dimer $[(CH_3)_2AuOH]_2$, and the formation constant is $\log {}^*\beta_{22} = -9.794 \pm 0.003$. This product is presumed to be structurally analogous to trimethylsiloxydimethylgold(III). The tetrameric molecule which has been identified in crystals of dimethylgold(III) hydroxide precipitated from aqueous solution is not present in significant concentrations. The equilibrium between $(CH_3)_2Au(OH_2)_2^+$ and $[(CH_3)_2AuOH]_2$ is rapid and reversible, but above pH 8 reaction appears to proceed very slowly.

Introduction

Hydrolysis reactions of metal ions have interested chemists for many years. There have been many efforts made to correlate information on the structures of the aquo cation, the hydrolyzed species in solution, and the hydroxide precipitate which eventually is obtained. In spite of this, the course of these reactions is still little understood. In most cases, the hydration numbers of the cations, *i.e.*, their coordination numbers with respect to oxygen in solution, are not known and the stoichiometry deduced for the soluble hydrolysis products generally shows no obvious relationship to the structure of solid products precipitated from the solutions. With the exception of Bi(III) and Pb(II), direct evidence bearing on the structures of the soluble hydrolysis products is lacking. With hydrolyzed bismuth and lead solutions where the cation stoichi-

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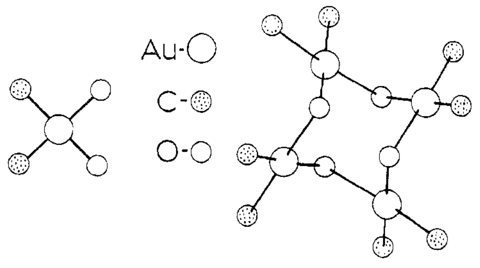
ometries are $Bi_6(OH)_{12}^{6+}$ and $Pb_4(OH)_4^{4+}$, X-ray scattering measurements[3,4] on the solutions have indicated cubic and tetrahedral symmetries, respectively, for the array of metal atoms. Little can be said about the positions of the hydroxo (or oxo) oxygens, since the scattering is almost entirely caused by the heavy-metal atoms.

Many deductions about the nature of hydrolyzed inorganic species have been based on the structures of olated complexes of substitutionally inert transition metal complexes. Even in these cases, detailed structural information has been available only recently. For example, the structure of the complex $[(H_3N)_4Co(OH)_2Co(NH_3)_4]Cl_4 \cdot 4H_2O$ synthesized by Werner in 1907 was first determined by Prout in 1962.[5] Recently the structure of $(H_3N)_3Co(OH)_3Co(NH_3)_3^{3+}$ was reported by Anderson.[6] The small size of oxygen leads to very short Co–Co distances in these compounds (2.93 and 2.55 Å, respectively) only slightly longer than those observed where direct cobalt–cobalt bonding is present. This factor makes the stability of these μ-hydroxo complexes surprising. The failure of fluoride ion to form di-μ bridges which are common with the heavier halogens is generally attributed to the small size of F^-.

Several years ago, we made a series of investigations of the hydrolysis of organotin compounds, *e.g.*, of $(CH_3)_2SnCl_2$, since these reactions were of interest in the synthesis of metallooxane polymers. It also was felt that blocking some of the coordination sites about the metal would limit the number of partially hydrolyzed species in solution, simplify analysis of the data, and permit more information on the nature of the hydrolysis reactions to be obtained. While this proved to be true, the stereochemistry of these organotin compounds was found to be quite variable making it difficult to establish the structures of the soluble polynuclear hydroxo complexes with any certainty.[7]

The alkyl derivatives of at least two transition metals give well-defined polymeric hydroxides, and both of these have structures related to that suggested for $Pb_4(OH)_4^{4+}$.[4,8] These are the dialkylgold(III) compounds, *e.g.*, $[(CH_3)_2AuOH]_4$,[9] and the trialkylplatinum(IV) compounds, *e.g.*, $[(CH_3)_3PtOH]_4$.[10,11]

The compounds containing $(CH_3)_2Au^{III}$ all exhibit basically square-planar coordination. Raman spectra of aqueous solutions of $(CH_3)_2AuClO_4$ and $(CH_3)_2AuNO_3$ indicate that the cation has the *cis* structure I.[12] Presumably there are two water molecules completing the square plane, and Au–O bond stretching vibrations are observed in the Raman spectra. However, these coordinated water molecules are exceedingly labile.[13] With all but very dilute solutions the tetrameric hydroxide II precipitates above a pH of *ca.* 6. The structure of the hydroxide involves *cis*-methyl groups and also basically square-planar coordination about the gold atom. The large ring structure of this tetrameric hydroxide leads to much longer Au–Au distances than presumably would be possible with di-μ-hydroxo bridges. It might also be noted that it is not possible for complexes with four nonbridging ligands, *e.g.*, $Co(NH_3)_4OH^{2+}$, to form puckered rings of this type because of the steric effects of the axial ammine groups.



I II

Experimental Section

Dimethylgold(III) Hydroxide.—This compound was synthesized by a modification of the procedure of Miles, *et al.*[12] Dimethylgold(III) iodide (10.5 g) was dissolved in 200 ml of petroleum ether (bp 60–68°) at room temperature. The clear solution was decanted from 60 mg of gray-brown residue and cooled to ice temperature. Ice water (25 ml) and then 148 ml of 0.2 *M* $AgNO_3$ in 0.01 *M* HNO_3 were added dropwise with stirring followed by a 10-ml excess. The petroleum ether was removed in a stream of nitrogen, and the aqueous slurry of AgI was collected on a frit. Sodium hydroxide (2 *M*) was added dropwise to the colorless filtrate until the brown color of Ag_2O just persisted in the white precipitate of $(CH_3)_2AuOH$. Nitric acid (2 *M*) was added until the brown color disappeared, and the hydroxide was collected on a frit, washed with cold water, and redissolved in 2 *M* HNO_3. Excess NaOH (2 *M*) was added to dissolve completely the $(CH_3)_2AuOH$, and the solution was filtered to remove *ca.* 60 mg of Ag_2O. The alkaline solution was diluted to 100 ml and back-titrated with 2 *M* HNO_3 to pH 8–10. The precipitate of dimethylgold(III) hydroxide was collected on a frit. A second crop of the hydroxide was collected by titrating the filtrate to pH 5. The product was washed with 20 ml of ice water and dried under vacuum at 10° over P_4O_{10}; yield, 92%. The hydroxide was recrystallized by dissolving it in benzene at 55°, filtering the solution to remove traces of colloidal gold, and storing the solution at 10°. A second crop of crystals was collected by reducing the filtrate to 60 ml; yield, 6.3 g, 88%. The compound was dried over P_4O_{10}. *It should be noted that while the hydroxide is insensitive when slightly moist, the dry material can be detonated upon occasion just by touching it.* *Anal.* Calcd for C_2H_7AuO: C, 9.84; H, 2.87; O, 6.59; Au, 80.7. Found: C, 9.97; H, 3.11; O, 6.33; Au, 80.3.

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Solutions.—Sodium perchlorate was prepared by neutralization of reagent Na_2CO_3, with reagent $HClO_4$. The solution containing excess $HClO_4$ was boiled to remove CO_2, neutralized to pH ~4, and filtered. The $NaClO_4$ was recrystallized twice, and the final product was free of chloride ion. The final stock solution was titrated to ensure that it contained neither excess free acid nor base. Dimethylgold(III) perchlorate solutions were prepared by dissolving finely powdered $[(CH_3)_2AuOH]_4$ in dilute standard perchloric acid by shaking for 24 hr. Perchloric acid solutions were standardized *vs.* sodium carbonate, and carbonate-free sodium hydroxide solutions were standardized against potassium hydrogen phthalate. Particular care was taken to prevent the introduction of any carbonate into the base solution.

Potentiometric Measurements.—The emf measurements were made using the Leeds and Northrup K-3 potentiometer–Cary 31V vibrating-reed electrometer circuit employed in other work from this laboratory. Beckman General Purpose and E-2 (lithium glass) electrodes were calibrated as hydrogen ion concentration probes in a 0.3 *M* $NaClO_4$ ionic medium. The cell (1) thermostated at 25° was used for the measurements.

$$\begin{array}{l}\text{glass}\\ \text{electrode}\end{array}\left|\begin{array}{l}[(CH_3)_2Au^+] = B\\ [H^+]\\ [Na^+] = 300\ \mathrm{m}M - [H^+] - B\\ [ClO_4^-] = 300\ \mathrm{m}M\end{array}\right\|$$

$$0.3\ M\ NaClO_4\left\|\begin{array}{l}[Cl^-] = 10\ \mathrm{m}M\\ [Na^+] = 300\ \mathrm{m}M\\ [ClO_4^-] = 290\ \mathrm{m}M\end{array}\right| AgCl \,|\, Ag \qquad (1)$$

Calculations.—All of the calculations were carried out with the University of Minnesota's CDC-6600 computer. In a typical experiment, an acidic solution containing B M $(CH_3)_2Au^{III}$ was titrated with equal volumes of solutions of NaOH and of an acidic solution $2B$ M in $(CH_3)_2Au^{III}$. In this way, the $(CH_3)_2Au^{III}$ concentration was maintained constant.

The input data for the computer program were the following: volume of solution being titrated, V_H; hydrogen ion concentration of solution being titrated, C_{acid}; concentration of $(CH_3)_2Au^{III}$ in solution being titrated, B; concentration of base in the first buret, C_{OH}; concentration of acid in the second buret, $C_{acid\text{-}B_2}$; concentration of $(CH_3)_2Au^{III}$ in the second buret, $C_{B\text{-}B_2}$; the titrant volumes for burets 1 and 2, V_{B_1} and V_{B_2}; the measured emf of cell 1, E; and the estimated errors in each of these quantities. The first part of the calculation was carried out by the FORTRAN program NBAR. This computes first the analytical hydrogen ion concentration **H**

$$\mathbf{H} = (V_H C_{acid} - V_{OH} C_{OH} + V_{B_2} C_{acid\text{-}B_2})/(V_H + V_{OH} + V_{B_2})$$

The quantity $E^{\circ\prime} = E - (RT/F)(\log\,[H^+])$ is then calculated either assuming $\mathbf{H} \approx [H^+]$ using points where the weak acid is essentially undissociated or if a provisional value of the first acid dissociation constant, $^*K_{11}$, is available from $[H^+] = [\mathbf{H} + (\mathbf{H}^2 + 4B^+K_{11})^{1/2}]/2$. The quantity E_j has been observed by many workers to be a constant in a perchlorate medium so long as $[H^+] \ll [ClO_4^-]$; *i.e.*, the cell emf's obey a relation $E = E^\circ + E_j[H^+] + (RT/F)(\log\,[H^+]) = E^{\circ\prime} + (RT/F)(\log\,[H^+])$. The data $E^{\circ\prime}$ *vs.* $[H^+]$ are fitted to a straight line by the method of least squares, the standard errors in E° and E_j are evaluated, and the best straight line $E^{\circ\prime} = E^\circ + E_j[H^+]$ is plotted. Initially the first 10 points at the beginning of the titration are used in this calculation and subsequently the first k points which satisfy the requirement $|(E^\circ + E_j[H^+]) - (E - (RT/F)(\log\,[H^+])| \leqslant 0.0001$ V. This procedure is employed to reject data automatically near the equivalence point for the titration of the excess strong acid where systematic analytical errors accumulate or where appreciable dissociation of the weak acid begins to occur. As a check on the analytical data, the end point for the titration of the excess strong acid by the base is determined by Gran's method.[14] A straight line was fitted by the method of least squares to the data $(V_{acid_i} + V_{OH_i})[\text{antilog}\ (F/RT)(E_i - E_j[H^+]_i)]$ *vs.* V_{OH_i} in order to determine the end point in the titration of the excess perchloric acid by the base. As a check on the analytical data, the normality of the base is calculated assuming that the acid concentration is correct, and *vice versa*. The final output from the program is: $\bar{n}_i$, the average number of protons transferred per mole of acid, $([H^+]_i - \mathbf{H}_i - (K_w/[H^+]_i))/B_i$; $\log\,[H^+]_i$; and $\sigma\bar{n}_i$, the estimated error in $\bar{n}$. The standard error in $\bar{n}$ is calculated from the estimated errors in the input quantities and the rules for propagation of variance. The data $\bar{n}(-\log\,[H^+])$ are plotted, and the values together with $\sigma_{\bar{n}}$ are also punched on cards to serve as input to the program GAUSS Z. This latter program for the least-squares refinement of equilibrium constants has been described in earlier publications,[15] and it minimizes the quantity $\Sigma_i w_i(\bar{n}_{i,\text{obsd}} - \bar{n}_{i,\text{calcd}})^2$. The weighting factor, w_1, was set equal to the reciprocal of the variances, $1/\sigma_{\bar{n}_i}{}^2$, in all of the calculations.[16]

Results

The data in the form of $\bar{n}$ as a function of $-\log\,[H^+]$ are illustrated in Figure 1. A preliminary titration of a ~2 m*M* solution of $(CH_3)_2AuClO_4$ in a 3 *M* $NaClO_4$ medium was reported earlier.[9] All of the data collected here are for a 0.3 *M* $NaClO_4$ medium because the solubility of $[(CH_3)_2AuOH]_4$ is very low in the more concentrated $NaClO_4$ solution. This low solubility limited the range of total $(CH_3)Au^{III}$ concentrations which could be employed to a twofold variation. Above 2.4 m*M*, precipitation occurred; below 1 m*M*, the experimental errors became intolerably large. In the acid–neutral range, $\bar{n}$ from 0 to 1, the reaction appeared to be complete within the time of mixing of the reagents, and constant potentials were attained quickly up to pH 7.5. Above $\bar{n} = 1$, the behavior is entirely different, and the potentials drifted indicating a slow decrease in pH although the system remained homogeneous. Up to pH ~10 where the standard glass electrode shows no appreciable sodium ion error, close agreement was obtained between the standard and lithium glass electrodes. Consequently, the drifting potentials probably reflect a real, slow consumption of base rather than electrode failure. Values of $\bar{n} = 2.4$ were reached at pH *ca.* 11, and traces of a precipitate occurred at this point.

These data differ from the preliminary measurements described earlier in one important way. Dimethylgold(III) is a weak acid and does not begin to dissociate appreciably until pH ~5.5. The earlier titration curve had a step, $\bar{n} = 0.5$ at pH ~3.0, which is absent in all of these measurements. This apparently resulted from an approximately 2 m*M* acidic impurity in the concentrated $NaClO_4$ solution used to adjust the perchlorate concentration. Also, there is a definite inflection at $\bar{n} = 1$. Aside from these, the titration curve shown earlier is approximately in agreement with the data reported here.

An examination of Figure 1 indicates that at least one of the hydrolysis products of $(CH_3)_2Au^+$ is polynuclear, *i.e.*, the $\bar{n}(\log\,[H^+])$ curves are shifted along the $\log\,[H^+]$ axis for different total $(CH_3)_2Au^{III}$

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[14] See, for example, the discussion in F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 54.

[15] R. S. Tobias and M. Yasuda, *Inorg. Chem.*, **2**, 1307 (1963).

[16] Flow sheets, deck listings, and card decks of the programs NBAR and GAUSS Z are available from R. S. T.

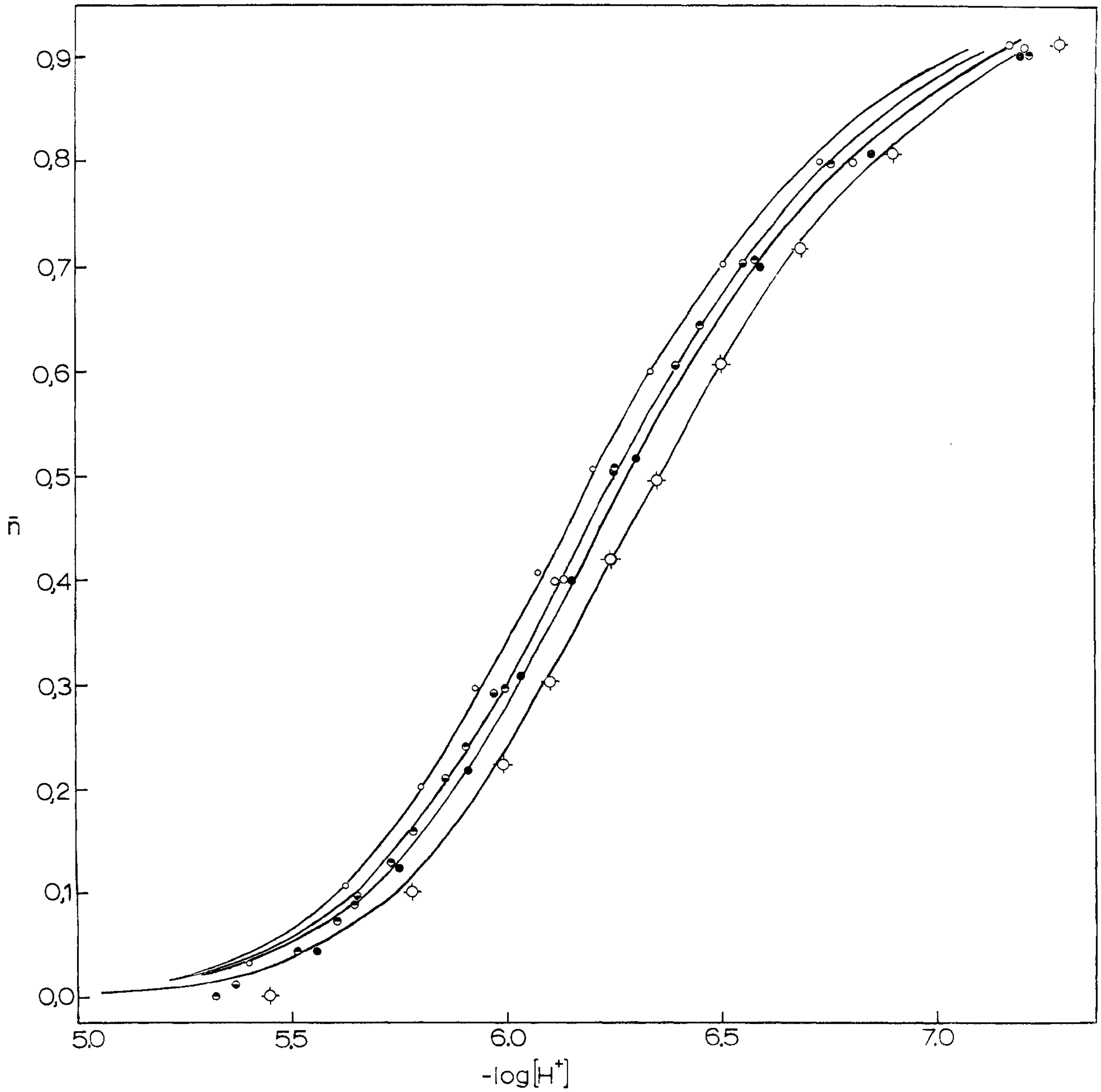

Figure 1. The average number of protons transferred per $(CH_3)_2Au^{III}$ as a function of $-\log [H^+]$. The diameter of the circles indicates the estimated error in $\bar{n}$ based on the analytical errors and the error in the emf measurements. The solid lines are drawn using $\log {}^*\beta_{22} = -9.79$: -⌽-, 0.0012 *M;* ●, 0.0017 *M;* ◓, 0.0019 *M;* ◒, 0.0019 *M* (duplicate); ○, 0.0024 *M* total $(CH_3)_2Au^{III}$ concentrations. Consequently the hydrolysis cannot be described in terms of monomeric $(CH_3)_2AuOH(OH_2)$ alone. On structural grounds, two products appear to be, most likely, a 4:4 complex, *i.e.*, $[(CH_3)_2AuOH]_4$ found in the X-ray study of the solid hydroxide precipitated from aqueous solution, and a 2:2 complex analogous in structure to the dimeric trimethylsiloxydimethylgold(III) found in the melt.[17]

Since the data are limited because of the low solubility of $[(CH_3)_2AuOH]_4$ and also are consistent with the predominance of a single soluble hydrolysis product, the initial calculations were made on this basis. Trial values of the equilibrium constants for 4:4, 3:3, 2:2, and 1:1, *i.e.*, the n:n complexes, were estimated from approximate solutions to the simultaneous equations

$$[H^+]_{\bar{n}=0.5}^{\,n} = n^*\beta_{nn}[(CH_3)_2Au^+]^{n-1}$$

$$B = [(CH_3)_2Au^+] + n^*\beta_{nn}[(CH_3)_2Au^+]^n[H^+]_{\bar{n}=0.5}^{\,-n}$$

In practice when only a single constant is involved, the Gauss-method calculation converges very rapidly even with very bad zero-order values of the equilibrium constant. As a result, the choice of initial value for the constant was not at all critical. The results of these calculations are collected in Table I together with values of $s^2 = \Sigma_i w_i(\bar{n}_{i,\mathrm{obsd}} - \bar{n}_{i,\mathrm{calcd}})^2/(N_0 - N_v)$; N_0 is the total number of data sets, 214, and N_v is the number of parameters being refined. Since s^2 gives an unbiased estimate of the variance and since the weights were set equal to $1/\sigma_{\bar{n}_i}^2$, the value of s^2 should be approximately unity when the correct hydrolysis product(s) has (have) been chosen. As anticipated, the fit is particularly bad, $s^2 = 62$, when only mono-

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[17] H. Schmidbaur and M. Bergfeld, *Inorg. Chem.*, **5**, 2069 (1966).

TABLE I

RESULTS OF THE LEAST-SQUARES REFINEMENTS FOR DIFFERENT POSTULATED HYDROLYSIS PRODUCTS

Complexes	Log of equilibrium constants[a]	$\Sigma_i w_i(\bar{n}_{i,\text{obsd}} - \bar{n}_{i,\text{calcd}})^2 / (N_0 - N_V)$
(1:1)	-6.28 ± 0.01	62.1
(2:2)	-9.79 ± 0.003	3.13
(3:3)	-13.15 ± 0.01	15.0
(4:4)	-16.45 ± 0.02	32.9
(2:2) + (4:4)	$-9.78 \pm 0.004, -19.4 \pm 0.1$	3.50[b]
(2:2) + (1:1)	$-9.78 \pm 0.02, -\infty$	3.19[c]

[a] Valid at 25° and in a 0.3 *M* ClO_4^- ionic medium. The nomenclature employed is that of the Chemical Society tables; *i.e.*, *K* is used for a stepwise equilibrium constant and *β* for a cumulative equilibrium constant: L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964. [b] Does not converge; log $^*\beta_{44}$ goes to $-\infty$ and s^2 goes to 3.55. Values listed are after 5 cycles. [c] Does not converge; log $^*\beta_{11}$ is reduced to $-\infty$.

meric dimethylgold(III) is assumed to be the product. By far the best fit was obtained assuming $[(CH_3)_2AuOH]_2$ to be the principal product, $s^2 = 3.1$. The value of the agreement factor, *s*, indicates that traces of other products are also formed or that the errors $\sigma_{\bar{n}_i}$ have been underestimated slightly. The latter case is distinctly possible, since there is no straightforward way to account for small systematic errors arising from an error in the cell $E°$ value. The agreement of the observed and calculated $\bar{n}$ values becomes progressively worse as products more highly polymerized than the dimer are assumed. Table II lists the observed $\bar{n}$ values and those calculated in the last cycle of the least-squares refinement.

Discussion

The dimethylgold(III)–aquo cation is a weak acid and transfers one proton in dilute solution over the pH range 5–7. It is comparable in strength to the unipositive trialkyltin(IV) cations, *e.g.*, $(CH_3)_3Sn^+$, log $^*K_{11} = -6.600$,[18] and it is appreciably weaker than CH_3Hg^+, log $^*K_{11} = -4.59$.[19] Both the methylmercury(II)[20] and dimethylgold(III)[12] cations in aqueous solutions give polarized Raman scattering at 463 and 418 cm^{-1}, respectively, assigned to metal–oxygen bond stretching vibrations indicating appreciable covalency in these bonds. With the trialkyltin(IV) cations, the intensity of the comparable Raman scattering is too low to be detected.[21] The effective charge neutralization brought about by the coordination of the alkyl groups may be noted by comparing the behavior of $(CH_3)_2Au^{III}$ to that of Au^{III}. The oxide, Au_2O_3, is virtually insoluble in concentrated $HClO_4$ and appears to dissolve in acids only when complex anions are formed.

TABLE II

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

MCONC	-LOG H	NOBS	NCAL	SIGN	MCONC	-LOG H	NOBS	NCAL	SIGN	MCONC	-LOG H	NOBS	NCAL	SIGN	MCONC	-LOG H	NOBS	NCAL	SIGN	MCONC	-LOG H	NOBS	NCAL	SIGN	MCONC	-LOG H	NOBS	NCAL	SIGN
1.946	4.750	-.038	.002	.007	1.950	6.875	.824	.845	.007	1.945	6.428	.630	.627	.007	1.683	6.265	.488	.485	.008	1.252	6.021	.243	.250	.011	2.408	5.795	.202	.195	.006
1.946	5.209	-.014	.016	.007	1.950	6.915	.835	.858	.007	1.945	6.469	.655	.653	.007	1.683	6.304	.517	.515	.008	1.252	6.046	.263	.267	.011	2.408	5.828	.226	.216	.006
1.947	5.325	0.000	.026	.007	1.950	6.957	.847	.870	.007	1.945	6.511	.679	.679	.007	1.683	6.326	.531	.532	.008	1.252	6.099	.303	.306	.011	2.408	5.878	.261	.249	.006
1.947	5.466	.029	.048	.007	1.951	7.053	.870	.894	.007	1.945	6.553	.703	.703	.007	1.683	6.366	.560	.561	.008	1.252	6.123	.322	.324	.011	2.408	5.893	.273	.259	.006
1.947	5.517	.043	.060	.007	1.951	7.110	.881	.907	.007	1.945	6.599	.727	.728	.007	1.683	6.386	.574	.576	.008	1.253	6.174	.361	.363	.011	2.407	5.924	.296	.282	.006
1.947	5.609	.072	.086	.007	1.951	7.230	.903	.928	.007	1.945	6.650	.751	.754	.007	1.683	6.426	.603	.604	.008	1.253	6.198	.380	.382	.011	2.407	5.954	.319	.304	.006
1.947	5.644	.087	.099	.007	1.951	7.315	.915	.941	.007	1.945	6.704	.775	.779	.007	1.683	6.448	.617	.619	.008	1.253	6.242	.420	.417	.011	2.407	5.983	.341	.325	.006
1.947	5.703	.115	.123	.007	1.951	7.410	.926	.952	.007	1.945	6.764	.799	.805	.007	1.683	6.493	.645	.648	.008	1.253	6.272	.438	.441	.011	2.407	6.012	.364	.348	.006
1.947	5.731	.129	.136	.007	1.951	7.520	.938	.963	.007	1.945	6.828	.822	.829	.007	1.683	6.516	.659	.663	.008	1.253	6.321	.477	.479	.011	2.407	6.042	.386	.372	.006
1.947	5.780	.158	.160	.007	1.945	7.368	.936	.947	.007	1.945	6.902	.845	.854	.007	1.683	6.565	.687	.692	.008	1.254	6.345	.496	.498	.011	2.407	6.071	.408	.394	.005
1.947	5.825	.186	.185	.007	1.945	4.631	-.037	.001	.007	1.945	6.998	.868	.881	.007	1.682	6.591	.700	.707	.008	1.253	6.397	.535	.537	.011	2.407	6.101	.430	.417	.006
1.948	5.912	.241	.241	.007	1.945	5.144	-.016	.012	.007	1.945	7.036	.879	.890	.007	1.682	6.646	.728	.736	.008	1.254	6.422	.552	.556	.011	2.407	6.131	.452	.441	.006
1.948	5.931	.255	.253	.007	1.945	5.367	.012	.032	.007	1.945	7.082	.891	.901	.007	1.682	6.675	.741	.751	.008	1.254	6.475	.590	.593	.011	2.407	6.173	.485	.474	.006
1.948	5.952	.269	.268	.007	1.945	5.486	.041	.053	.007	1.945	7.214	.913	.926	.007	1.682	6.736	.769	.780	.008	1.254	6.503	.608	.613	.011	2.407	6.203	.506	.497	.006
1.948	5.990	.296	.296	.007	1.945	5.578	.070	.076	.007	1.685	5.054	-.035	.007	.008	1.682	6.772	.782	.795	.008	1.255	6.562	.645	.651	.011	2.407	6.235	.528	.522	.006
1.948	6.028	.323	.325	.007	1.945	5.649	.098	.101	.007	1.685	5.363	-.021	.027	.008	1.682	6.845	.809	.824	.008	1.255	6.586	.663	.667	.011	2.407	6.265	.549	.544	.005
1.948	6.097	.377	.378	.007	1.945	5.709	.127	.125	.007	1.685	5.506	.027	.050	.008	1.682	6.887	.822	.838	.008	1.255	6.624	.682	.689	.011	2.407	6.308	.580	.576	.006
1.948	6.062	.350	.351	.007	1.945	5.766	.155	.153	.007	1.685	5.562	.043	.063	.008	1.682	6.978	.849	.867	.008	1.255	6.691	.718	.727	.011	2.407	6.339	.601	.597	.005
1.948	6.131	.403	.405	.007	1.945	5.811	.183	.177	.007	1.685	5.647	.075	.088	.008	1.682	7.023	.862	.879	.008	1.255	6.725	.736	.744	.011	2.407	6.369	.621	.618	.005
1.948	6.165	.429	.432	.007	1.945	5.856	.211	.204	.007	1.684	5.684	.091	.102	.008	1.682	7.138	.889	.906	.008	1.255	6.764	.754	.763	.011	2.407	6.402	.642	.640	.006
1.949	6.197	.455	.457	.007	1.945	5.878	.225	.218	.007	1.684	5.750	.123	.130	.008	1.682	7.204	.902	.918	.008	1.255	6.846	.790	.800	.011	2.407	6.436	.662	.661	.006
1.949	6.230	.481	.483	.007	1.945	5.899	.239	.232	.007	1.684	5.780	.139	.144	.008	1.682	7.372	.928	.944	.008	1.256	6.896	.806	.819	.011	2.407	6.470	.682	.682	.006
1.949	6.265	.507	.510	.007	1.945	5.936	.266	.257	.007	1.684	5.836	.170	.174	.008	1.682	7.484	.941	.956	.008	1.256	6.948	.825	.838	.011	2.407	6.507	.702	.703	.006
1.949	6.300	.532	.536	.007	1.945	5.971	.293	.282	.007	1.684	5.862	.186	.189	.008	1.250	5.061	-.038	.005	.011	1.256	6.996	.843	.853	.011	2.407	6.546	.722	.725	.006
1.949	6.339	.558	.565	.007	1.945	6.004	.321	.306	.007	1.684	5.908	.217	.217	.008	1.250	5.305	-.020	.016	.011	1.256	7.120	.878	.887	.011	2.407	6.589	.742	.747	.006
1.949	6.373	.583	.589	.007	1.945	6.040	.347	.334	.007	1.684	5.931	.233	.232	.008	1.251	5.451	-.000	.030	.011	1.256	7.212	.895	.908	.011	2.407	6.631	.761	.757	.007
1.949	6.412	.608	.616	.007	1.945	6.076	.374	.361	.007	1.684	5.974	.264	.262	.008	1.251	5.555	.020	.047	.011	1.256	7.294	.913	.923	.011	2.407	6.677	.781	.788	.007
1.949	6.452	.633	.642	.007	1.945	6.109	.400	.387	.007	1.684	5.995	.279	.276	.008	1.251	5.627	.041	.063	.011	1.256	7.399	.930	.939	.011	2.407	6.728	.800	.809	.007
1.950	6.493	.656	.668	.007	1.945	6.142	.427	.413	.007	1.684	6.034	.309	.305	.008	1.251	5.695	.061	.083	.011	2.408	5.401	.032	.045	.006	2.407	6.782	.819	.829	.007
1.950	6.537	.681	.695	.007	1.945	6.183	.453	.446	.007	1.684	6.051	.324	.318	.008	1.251	5.741	.081	.099	.011	2.408	5.487	.057	.064	.006	2.407	6.846	.838	.850	.007
1.950	6.583	.706	.720	.007	1.945	6.212	.479	.468	.007	1.684	6.091	.355	.349	.008	1.251	5.786	.102	.117	.011	2.408	5.560	.082	.085	.006	2.407	6.914	.857	.871	.007
1.950	6.632	.730	.745	.007	1.945	6.247	.504	.496	.007	1.683	6.109	.370	.363	.008	1.251	5.828	.122	.136	.011	2.408	5.619	.106	.107	.006	2.407	6.986	.875	.889	.007
1.950	6.685	.753	.771	.007	1.945	6.281	.530	.522	.007	1.683	6.146	.399	.392	.008	1.251	5.865	.143	.154	.011	2.408	5.669	.130	.128	.006	2.407	7.074	.894	.909	.007
1.950	6.740	.777	.795	.007	1.945	6.318	.555	.549	.007	1.683	6.185	.429	.423	.008	1.252	5.900	.163	.173	.011	2.408	5.717	.155	.151	.006	2.407	7.171	.912	.926	.007
1.950	6.772	.789	.808	.007	1.945	6.354	.581	.575	.007	1.683	6.204	.444	.438	.008	1.252	5.934	.183	.193	.011	2.408	5.756	.179	.172	.006	2.407	7.293	.930	.944	.007
1.950	6.805	.800	.821	.007	1.945	6.390	.605	.601	.007	1.683	6.244	.473	.469	.008	1.252	5.992	.223	.230	.011										

[a] All dimethylgold(III) concentrations are in millimoles per liter.

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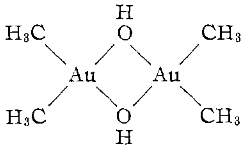
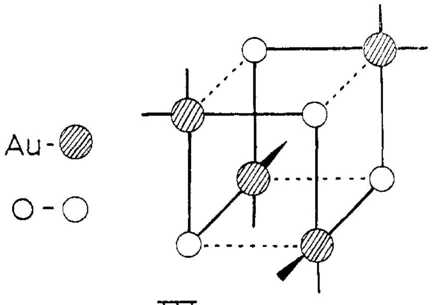
The predominant soluble hydrolysis product has the stoichiometry $[(CH_3)_2AuOH]_2$, and it is reasonable to presume that this has the same bridged structure III as the dimethylgold(III) halides and trimethylsiloxydimethylgold(III).[17] The freshly precipitated hydroxide may have a structure different from that of the crystal studied by X-ray diffraction[9] which was obtained by recrystallization from a benzene solution. Nevertheless, it seems likely that both of these crystalline forms contain the tetramer II, since both exhibit in a variety of organic solvents the two equal-intensity methyl proton magnetic resonances which appear to be characteristic of the tetramer. In addition both of the crystalline modifications obtained from benzene solution, *i.e.*, the plate- and needlelike crystals,[9] give identical methyl resonances in chloroform solution. This tetramer is not a significant aqueous solute species. Relatively strong solvation of the hydroxide may be responsible for the stability of the dimer in dilute aqueous solutions. The stability of the dimer is surprising, since rather strong gold–gold repulsions would be expected with the four-membered ring. Because of the rather hydrophobic character presented by the eight methyl groups, the tetramer would not be expected to be very soluble in water. The stability of the tetramer over the dimer in the crystalline state may be related to the very efficient packing of these large molecules in the solid state[9] and the diminution of the gold–gold interactions.



III



IV

An idealized drawing of the structure of $[(CH_3)_2AuOH]_4$ is shown in structure IV. The tetramer could be produced from two dimers by distortion of one Au–O bond in each from *ca.* 2.2 to 3.6 Å which is close to the sum of the van der Waals radii of oxygen (1.40 Å) and gold (2.2 Å)[22] together with the formation of a like number of new strong Au–O bonds linking the dimers together. All indications point to high lability for ligands bound to organometallic cations and very low stereochemical rigidity for most of these compounds, so such a process is not unreasonable. For example, the mean lifetime of a water molecule bound in the first coordination sphere of the dimethylgold(III) cation is of the order of 10^{-5} sec at room temperature.[13]

Considering that the dimer is formed rapidly and reversibly, the slowness of the reaction which occurs above pH 8 is surprising. There is no indication of any cleavage of the gold–carbon bonds, for the solutions remained clear and colorless. Even when $[(CH_3)_2AuOH]_4$ is dissolved is aqueous NaOH so that the solution produced contains *ca.* 1 *M* OH^-, there is no indication from either the pmr or Raman spectra of the solutions that any destruction of the $(CH_3)_2Au^{III}$ moiety has occurred.[12] It appears that the polycondensed hydroxide is only slowly attached by nucleophiles such as OH^-. Not only is the dimer apparently rather resistant to attack by OH^-, but this complex is also thermodynamically very stable relative to the monomer. The equilibrium constant for dimerization of $(CH_3)_2AuOH(aq)$ must be larger than 10^3, or it would have been possible to detect traces of the monomer. Hydroxo groups bound to a metal are still very effective electron donors.

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