The ionization of COOH radical could certainly explain the rapid increase in rate as pH increases from 0.55 to 4.5. From the midpoint of the left half of the curve in Figure 1, a pK value of 2.8 is determined for reaction 13 with the assumption that other factors are relatively unimportant in this region.

The explanation at high pH invoking the ionization of HO_2 radical to O_2^- radical[23] is not very likely in the uncatalyzed oxalate–peroxodisulfate reaction where there is no evidence that HO_2 is produced. There is no reason to believe that the phosphate buffer complicates the reaction at high pH since it is known to be not susceptible to attack by free radicals. Also, a few experiments at low pH where phosphate buffer was employed gave the same results as those in the absence of phosphate. All attempts to develop a sound explanation failed, and it seems likely that more than one factor contributes to the reduction in rate in the high pH range.

Many reactions exhibit specific salt effects, and in many instances the effects arise under conditions where ion pairing of the oppositely charged ions occurs in the reacting mixtures. The catalytic effect of added salts in the alkali metal ions is found to increase in the order $Li^+ < Na^+ < K^+$. To explain these effects, the concepts of ion pairing and the relative degree of hydration of the counterions are invoked.

In the present work, potassium and sodium ions are found to enhance the rate of oxidation of oxalate by peroxodisulfate with the former cation exerting a stronger effect. Reaction 6 is an electron-transfer process involving two reactive free-radical species, and it should not be affected by the presence of counterions. It is reasonable to assume that reaction 5 is subject to the catalytic effect of the cations. The alkali metal cations may reduce the unfavorable coulombic repulsion in reaction 5 by forming ion pairs with the anions. The stronger enhancement of the rate by K^+ than by Na^+ is likely due to the greater ability of K^+ to form ion pairs with the anions in solution.[27]

Acknowledgments. The authors wish to express their appreciation to John L. Voth for technical assistance. The financial assistance of a research grant from the National Science Foundation is gratefully acknowledged.

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(27) C. W. Davies, "Ion Association," Butterworth and Co., Ltd., London, 1962.

The Crystal and Molecular Structure and the Solution Conformation of Dimethylgold(III) Hydroxide, an Inorganic Intermediate Ring Compound[1]

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Abstract: Dimethylgold(III) hydroxide has been found to be a tetrameric molecule in the crystalline state by three-dimensional X-ray crystal structure analysis and also in benzene solution by vapor pressure osmometry. There are 32 monomeric formula units in the orthorhombic unit cell in space group Pbca with $a = 19.35 \pm 0.03$, $b = 9.65 \pm 0.02$, and $c = 19.59 \pm 0.03$ Å. The gold, carbon, and oxygen atoms were located by Patterson and Fourier methods. The molecule consists of an eight-membered ring unlike that of any other known gold(III) compound. Gold achieves the expected square-planar coordination *via* bridging hydroxo oxygens, and the molecule has the approximate symmetry S_4. The final structure, with gold atoms refined by anisotropic least squares and with light atoms determined from Fourier maps, had a conventional R of 0.091. The mean bond lengths (with average deviations from the mean) are Au–C = 2.05 ± 0.08 Å and Au–O = 2.15 ± 0.12 Å. The rings stack together in columns; the short oxygen–oxygen contacts of 2.74 Å and the infrared spectrum both indicate strong intermolecular hydrogen bonding. These columns, in turn, pack together tightly to give a very compact structure. In solution, the molecule apparently is stereochemically rigid, and pmr measurements on solutions indicate that the two kinds of methyl groups required by the S_4 symmetry are still magnetically nonequivalent up to at least 94°. Strong axial interactions of the predominantly square-planar d^8 gold(III) may be responsible for the rigidity of the molecule in solution. This is supported by the observation that the dimethylgold(III) aquo ion behaves like a triprotic acid.

Recently, we reported the synthesis of dimethylgold(III) hydroxide.[4] The compound is only very slightly soluble in water but dissolves readily in aqueous acids and bases. The fact that it is moderately soluble in many organic solvents indicates a covalent structure. When this compound was first isolated, we assumed that it would have a symmetrical dimeric structure analogous to the dimethylgold(III) halides.[5] The organ ocompounds of gold(III) are similar in many of their reactions to organoplatinum(IV) compounds, and Morgan, Rennick, and Soong have presented evidence recently that $[(CH_3)_3PtCl]_4$ and $[(CH_3)_3Pt(OH)]_4$

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(2) (a) NASA Trainee, 1964–1967; (b) American Oil Corp. Fellow; (c) Research Fellow in Chemistry.

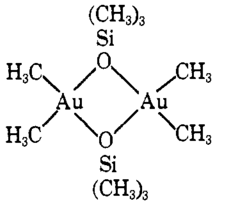
(3) Author to whom correspondence should be addressed.

(4) M. G. Miles, G. E. Glass, and R. S. Tobias, *J. Am. Chem. Soc.*, **88**, 5738 (1966).

(5) See, for example, A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 884.

are isostructural.[6] The idea of a symmetrical binuclear structure for the hydroxide had to be abandoned at once, however, since the pmr spectra with a variety of solvents all showed two signals of equal intensity for the protons in methyl groups bound to gold.

In contrast to the behavior of the hydroxide, trimethylsiloxydimethylgold has been reported recently to be dimeric in benzene solution.[7] The symmetrical structure I, analogous to the structures of the dimethylgold(III) halides, is consistent with cryoscopic measurements on benzene solutions and with the pmr and infrared spectra. The pmr spectrum shows two singlet signals with the relative areas of 3:2 for the methyl groups bound to silicon and gold, respectively.



I

This paper reports a detailed investigation of the structure of dimethylgold(III) hydroxide both in the crystalline state and dissolved in organic solvents.

Experimental Section

Preparation of Dimethylgold(III) Hydroxide. This compound was synthesized by the procedure described earlier.[4] The product which was precipitated from aqueous solution was dried over P_4O_{10} in a vacuum desiccator at room temperature and then recrystallized from benzene. Well-developed needle-like crystals were obtained by evaporation of the solvent from a benzene solution stored in a refrigerator. A small number of plate-like crystals also grew from the solution, and these were separated from the needles which were used in the studies described below. *Anal.* Calcd for C_2H_7AuO: C, 9.84; O, 6.55; H, 2.87; Au, 80.7. Found: C, 9.55; O, 6.46; H, 2.80; Au, 81.0. The compound tends to detonate during combustion analyses,[8] and it also explodes upon rapid heating.

Equivalent and Molecular Weight Determinations. The equivalent weight of the recrystallized dimethylgold(III) hydroxide was determined as part of a preliminary study of the hydrolytic behavior of $[(CH_3)_2Au]^+$. Stock solutions of this cation as the perchlorate salt were prepared by dissolving weighed samples of $(CH_3)_2AuOH$ in standard perchloric acid. The titration curves showed a distinct break corresponding to the neutralization of the excess perchloric acid and one proton from the dimethylgold(III) aquo ion. All titrations were carried out at 25° in a constant ionic medium with $[ClO_4^-] = 3$ *M*. The techniques were similar to those used for other hydrolysis studies in this laboratory.[9] The average of three determinations of the equivalent weight was 249 ± 12 (calculated, 244.1).

Molecular weight data for the dimethylgold(III) hydroxide were obtained with a Mechrolab vapor pressure osmometer, Model 301 A. The samples were run in benzene solution at 37°, and the average of two independent series of measurements gave the molecular weight 828 ± 35.[10] This corresponds to a number-average degree of polymerization of $(CH_3)_2AuOH$ of $3.4_0 \pm 0.1_4$. Because the compound decomposed at elevated temperatures, it was vacuum dried over P_4O_{10} at room temperature for a period of weeks prior to these measurements. In spite of this treatment, pmr spectra of benzene solutions of the compound indicated that there was still *ca.* 0.05 mole of free water per mole of $(CH_3)_2AuOH$ in the benzene solutions. The presence of this trace of free water was confirmed by infrared spectra of chloroform solutions. When the molecular weight measurements are corrected for this amount of dissolved water, the number-average degree of polymerization becomes 4.0 ± 0.3. These measurements indicate how difficult it is to obtain reliable values for compounds with such large molecular weights (976.18 in this case).

Infrared and Pmr Spectra. Infrared spectra were obtained with a Perkin-Elmer Model 521 grating spectrometer using the split mull technique and KBr and CsI windows and liquid cells with KBr windows. Calibration of the instrument was effected with polystyrene film. The pmr spectra were obtained with a Varian A-60 spectrometer, and the coupling constants and chemical shifts are believed to be accurate to ±1.0 cps and ±0.02 ppm, respectively. The chemical shifts were measured relative to the internal standard tetramethylsilane, TMS.

Unit Cell and Space Group. Precession photographs were taken with Mo Kα (0.7107 Å) and Weissenberg photographs were taken with Cu Kα (1.5418 Å) radiation. The crystals are orthorhombic with $a = 19.35 \pm 0.03$, $b = 9.65 \pm 0.02$, and $c = 19.59 \pm 0.03$ Å, and the space group is Pbca.[11] The crystals grow as needles with *b* the needle axis and with the forms $\{100\}$ and $\{102\}$ well developed The ends of the needles do not form faces that can be indexed. As shown by the structure determination, there are 32 monomeric formula units per unit cell; the calculated density is 3.54 g/cm³.

Equiinclination Weissenberg multiple film photographs were obtained for the *h*0*l*–*h*5*l* zones, and the precession pictures were taken of the *hk*0 and 0*kl* zones. The crystals used were approximately 0.08 × 0.04 × 4 mm. Each crystal was used for two 24-hr Weissenberg photographs before decomposition in the X-ray beam rendered it useless. The intensities of 539 independent observable reflections were measured by visual comparison to a scale prepared by exposing a chosen reflection for known lengths of time. This is a rather small number of reflections for a unit cell this large; only 15% of the reflections in the Cu Kα limiting sphere were observed. The fragility and shape of the crystals precluded data collection around another axis, and the decomposition and large thermal parameters precluded the observation of higher angle reflections on the layers collected. The intensities were corrected for the Lorentz and polarization factors, and absorption corrections were made including allowance for crystal shape ($\mu = 599$ cm^{-1} for Cu Kα). The transmission coefficients varied from 0.04 to 0.15; Mo radiation, which would have been absorbed less, was ruled out by the larger exposure time required, since the crystal decomposed fairly rapidly in the X-ray beam. The Weissenberg layers were correlated with the precession data.

The absorption corrections were made using a local modification of the GNABS program of C. W. Burnham. The Fourier and least-squares calculations were made using programs provided by Mr. Larry Finger of the Geology Department of the University of Minnesota. All calculations were made on either the CDC 1604 or 6600 computers of the Numerical Analysis Center of the University of Minnesota.

No information could be obtained for the plate-like crystals, because they decomposed rapidly in the X-ray beam.

Results

Figure 1 shows the pmr spectra of dimethylgold(III) hydroxide in benzene and chloroform solution. These spectra are typical of those obtained with a variety of solvents. Table I summarizes the pmr data.

All of the spectra showed two intense methyl proton signals in the range τ 8.71–9.29 which were of equal area. A melt of trimethylsiloxydimethylgold is reported to show a single methyl resonance at τ 9.04[12] for the

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[6] G. L. Morgan, R. D. Rennick, and C. C. Soong, *Inorg. Chem.*, 5, 372 (1966).

[7] H. Schmidbaur and M. Bergfeld, *ibid.*, 5, 2069 (1966).

[8] Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[9] See, for example, C. E. Freidline and R. S. Tobias, *Inorg. Chem.*, 5, 354 (1966).

[10] We are indebted to Dr. D. P. Eyman of the University of Iowa for these measurements.

[11] The space group was indicated by the requirements: for 0*kl*, $k = 2n$; for *h*0*l*, $l = 2n$; for *hk*0, $h = 2n$. In addition, there were two approximate requirements; for *h*0*l*, $2h + l = 4n$; for *hk*0, $k = 2n$. These proved to arise from the coincidence that an approximate two-fold axis of the tetramer was parallel to *b* at $x \sim {}^1/_4$, $y \sim {}^1/_8$. This led to no problems with three-dimensional data, but projections, which were used at first, could be interpreted either in Pbca or in Pbcn. In both space groups, for the same reason, there were two possible solutions, which differed only in the packing of the adjacent columns. The very slightly idealized structure, therefore, provides an example where three complete two-dimensional projections do not allow a decision among four different three-dimensional structures.

[12] This assumes measurement at 60 Mc/sec, since the frequency was not given in the reference.

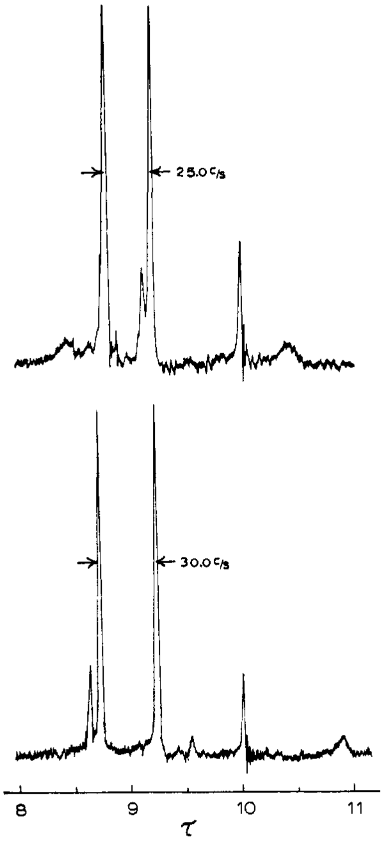

Figure 1. Proton magnetic resonance spectra of [$(CH_3)_2AuOH]_4$: upper spectrum, benzene solution; lower spectrum, chloroform solution.

methyls bound to gold.[7] The carbon-13 proton coupling constants as measured with the benzene solution of $(CH_3)_2AuOH$ at 72° were identical for the two signals, $J_{^{13}C-H} = 138 \pm 1$ cps. The benzene solutions always showed two additional, weak signals at τ 10.9 and 8.63 ppm. The signal at 10.9 ppm is similar to that observed for free hydroxo protons of trimethylplatinum(IV) hydroxide at 11.5 ppm,[6] but it is very broad. The signal at 8.63 ppm was identified as arising from water bound to the solute species. Known amounts of water were introduced with an ultramicroburet, and the 8.63-ppm signal increased in intensity as up to *ca.* 1 mole of water per $(CH_3)_2AuOH$ formula unit was added. The addition of more water led to a signal at 9.55 ppm characteristic of water dissolved in benzene. The ratio of the integral of the 10.9-ppm signal to the sum of the 9.23 + 8.71 ppm signals was *ca.* 1:6. The area of the 8.63-ppm signal relative to that of the 9.23 + 8.71 ppm integral varied somewhat from sample to sample but was usually *ca.* 1:6. In DMSO solutions, the dissolved water and bound water signals broadened and merged as the temperature was raised from 70 to 94°.

Table I. Pmr Spectra of Dimethylgold(III) Hydroxide at 40° (τ(TMS) = 10)

Solvent	$\tau(H_3C-Au)^a$	τ(HO–Au)	τ(other protons)
C_6H_6	9.23, 8.71	10.9[b]	9.55,[c] 8.63[d]
$CHCl_3$	9.19, 8.78	10.5[b]	9.10,[d] 8.74, 8.45[c]
CH_2Cl_2	9.18, 8.79	...[e]	8.72
CCl_4	9.25, 8.84	...[e]	8.79
$C_2H_4Br_2$	9.23, 8.83	...[e]	9.00
$C_6H_5NO_2$	9.10, 8.74	...[e]	8.80, 8.70
$(CH_3)_2CO$	9.25, 8.87	...[e]	9.20, 7.20[c]
$(CH_3)_2SO$	9.29, 8.97	...[e]	9.21, 8.93,[d] 6.70[c]

[a] Signals of equal area. [b] Broad signals. [c] Dissolved water. [d] Bound water. [e] Solutions too dilute to observe.

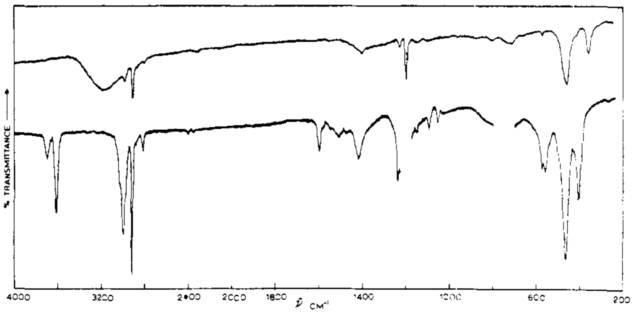

Figure 2. Infrared spectra of [$(CH_3)_2AuOH]_4$: upper spectrum, mull; lower spectrum, chloroform solution with solvent in the reference beam.

The intensity of the two signals assigned to methyl groups bound to gold, measured relative to an internal TMS standard, did not vary with temperature in benzene solution up to the solvent boiling point of 80°, in DMSO up to 94°, or in methylene chloride solution down to −81°. This indicates that the tetramer does not dissociate appreciably in solution.

Figure 2 shows the infrared spectrum of the $(CH_3)_2AuOH$ needles, and Table II lists the band frequencies. Values are also given for trimethylsiloxydimethylgold and for the Raman-active vibrations of $(CH_3)_2AuOH$ dissolved in strong aqueous base. The assignments are based on the work of Miles, Glass, and Tobias.[4]

The vibrational frequencies observed for the hydroxide are similar to those found for the anionic species obtained by dissolution of the hydroxide in base. The lower frequency vibrations are also quite similar to those reported for the dimeric trimethylsiloxydimethylgold. The crystal spectra show a broad band characteristic of hydrogen-bonded O–H bond stretching. In $CHCl_3$ solution, this disappears and a medium band appears at 3687 cm^{-1} and a stronger one at 3601 cm^{-1}. The former is characteristic of water dissolved in chloroform as is the band observed for the solutions at 1598 cm^{-1}. In addition to the observation that two different kinds of crystals could be obtained by slow evaporation of benzene solutions of the hydroxide, the infrared spectra also indicated that different crystal modifications could be obtained. Crystallization by chilling a hot, saturated benzene solution of the hydroxide gave a powder with a considerably different spectrum from that of the needle-like crystals. Mulls gave an OH stretching band at 3598 cm^{-1} typical of nonhydrogen-bonded OH stretching, and the lower frequency bands were split giving a much more complex spectrum.

The data from titrations of 2 m*M* solutions of $(CH_3)_2AuClO_4$ are illustrated in Figure 3 as the average number of protons transferred per dimethylgold(III), $\bar{n}$, as a function of pH. The hydroxide can be precipitated from more concentrated aqueous solutions by adjusting the pH of either an acidic or an alkaline solution to the region pH 4–5.5. Up to pH 9, the ion behaves like a

Table II. Assignment of Fundamentals for Dimethylgold(III) Compounds[a]

$\nu[(CH_3)_2AuOH]_4$ (ir, mull), cm^{-1}	$\nu[(CH_3)_2AuOH]_4$ (ir, $CHCl_3$ soln), cm^{-1}	$\nu[(CH_3)_2AuOSi(CH_3)_3]_2$[b] (ir) cm^{-1}	$\nu[(CH_3)_2Au(OH)_n]^{(1-n)+}$[c] (R), cm^{-1}	Assignment
	3687 m			H_2O
	3602 s			Au–OH
3100–3400 s				Au–OH
2978 w	2986 s	. . .[d]	3004	CH_3 antisym stretch
2910 s	2910 s		2914	CH_3 sym stretch
2860 vw		. . .[d]		
2806 vw	2808 w			
	1598 w			H_2O
1410 w, bd	1418 w	. . .[d]		CH_3 antisym def
1263 w		1258		CH_3 sym def
1233 w	1239 w	1245	1249	
1206 m		1210	1220	
579 m	575 m	588	586	Au–C stretch
	562 m	577		
468 s	466 s	478	441	Au–O stretch ring modes
317 m	410 m			

[a] w, weak; m, medium; s, strong; v, very; bd, broad; ir, infrared; R, Raman. [b] Data from ref 7. [c] Data from ref 4; $n \geq 3$. [d] Not reported.

triprotic acid. Further work is underway to determine if polynuclear species are present in appreciable concentration in the aqueous solutions. From the pH corresponding to $\bar{n} = 0.5$, an upper limit of 10^{-3} can be estimated for the first acid dissociation constant of the dimethylgold(III) aquo ion.

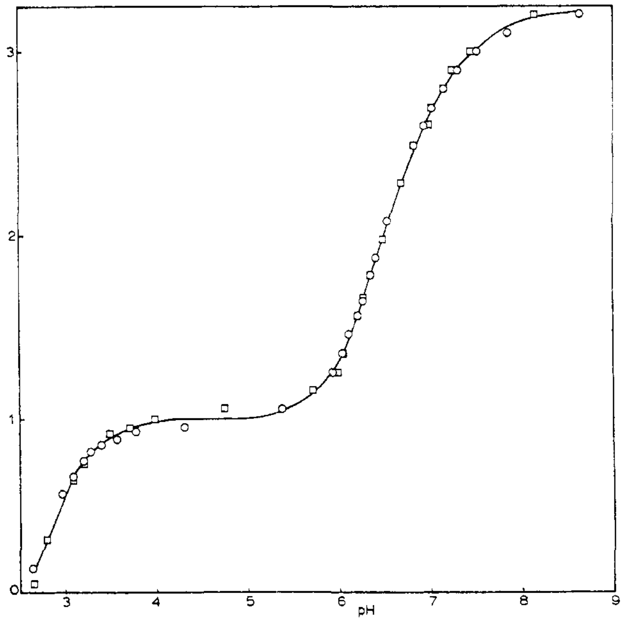

Figure 3. Average number of protons transferred per $(CH_3)_2Au^{III}$ as a function of pH.

Determination of the Crystal Structure

The positions of the gold atoms were determined from Patterson projections and refined by least squares (isotropic thermal parameters). Least squares was carried out on the numerator of the function $r = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$ with the resulting values of R ($R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$) and r both equal to 0.15. A difference Fourier map was then prepared from which the approximate light-atom positions were determined. The peaks chosen for the light atoms were the 12 highest on the map. At this point the scale factors for the Weissenberg layers were smoothed so that ln K_k *vs.* k^2 gave a smooth curve, where k is the Miller index of the Weissenberg layer, and K_k is the scale factor that minimizes r for that layer.

Using the light-atom positional parameters from the difference Fourier map, with carbon and oxygen having isotropic temperature factors of 7.0 and 6.0, respectively, the positional and anisotropic thermal parameters of the gold atoms were refined giving $R = 0.118$ and $r = 0.095$.[13] New light-atom positions were then taken from a difference Fourier map where only the anisotropically refined gold atoms determined the calculated structure factors and the sign of the Fourier coefficients. The single structure factor that changed sign with the inclusion of the light atoms was omitted. Owing evidently to series termination, the difference Fourier map gave better shaped light-atom peaks than did a regular Fourier map based on all atoms.

At this point, 13 of the reflections (those marked with asterisks in Table V) contributed approximately 30% of r. In the subsequent refinements, these reflections were given zero weight. In this way, they were included in R but not in r. (After the final refinement, roughly half of the 13 omitted reflections had moved into much closer agreement with the corresponding calculated structure factors and might have been included in a further refinement. The other half, all faint reflections, still would have made an unreasonably large contribution to r.) The weighting scheme used from this point on was $w = 1.0$ for $F_o < 120$ and $w = (120/F_o)^4$ for $F_o > 120$.

Full-matrix least-squares refinement was carried out using the 526 reflections with nonzero weights. The

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(13) Scattering factors for the neutral atoms were taken from "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962, p 201 (C and O) and p 212 (Au). Anomalous dispersion corrections were not included in any of the calculations reported above. At the suggestion of a referee, the refinement was repeated including anomalous dispersion corrections ("International Tables", p 215). The largest changes in the positional parameters were less than 0.2σ for Au and 0.25σ for O and C. The changes in the positions of the light atoms from the difference Fourier map were similarly small. In view of the smallness of the changes, the original results, given in the tables and the figures, were not changed to the values from the refinement including anomalous dispersion.

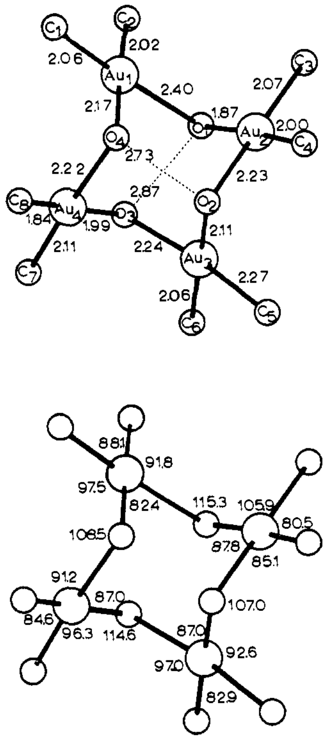

Figure 4. Bond lengths and bond angles of $[(CH_3)_2AuOH]_4$.

Table III. Final Atomic Positional Parameters in $[(CH_3)_4AuOH]_4$ with Their Estimated Standard Deviations in Parentheses[a]

Atom	x	y	z
Au(1)	0.1974 (0.0002)	0.2754 (0.0007)	0.0072 (0.0008)
Au(2)	0.3656 (0.0002)	0.3479 (0.0006)	0.0797 (0.0002)
Au(3)	0.2942 (0.0002)	0.2714 (0.0007)	0.2390 (0.0008)
Au(4)	0.1286 (0.0002)	0.3543 (0.0005)	0.1712 (0.0002)
O(1)	0.298	0.210	0.071
O(2)	0.305	0.433	0.167
O(3)	0.200	0.207	0.181
O(4)	0.191	0.435	0.085
C(1)	0.116	0.342	−0.052
C(2)	0.215	0.127	−0.063
C(3)	0.429	0.328	−0.005
C(4)	0.428	0.510	0.095
C(5)	0.380	0.357	0.306
C(6)	0.285	0.129	0.317
C(7)	0.079	0.317	0.265
C(8)	0.068	0.500	0.164

[a] The light-atom position were determined from the final difference Fourier map. No estimates of the standard deviations of these positions were made from the map.

gold thermal parameters were anisotropic, and the light atoms were fixed at their difference Fourier map positions with fixed isotropic temperature factors of 6.0 for the oxygens and 7.0 for the carbons. For this refinement $r = 0.0481$ and $R = 0.0907$. A least-squares refinement of all atom positions and temperature factors was then carried out with anisotropic thermal parameters for the golds and isotropic parameters for the light atoms. For this refinement, $r = 0.0419$ and $R = 0.0888$. In both cases, refinement was continued until all shifts were less than the associated standard deviation. Hamilton's R factor ratio test[14] says that, if we reject the hypothesis that the light-atom positions are the difference Fourier map values with the stated temperature factors, the probabliity of error is about 10%. Rejection is not demanded at this level. Since the positions from the difference Fourier map showed less scatter in the carbon-gold distances than did the least-squares positions, the former were chosen. Table III gives the positional parameters of the atoms and their standard deviations. The bond lengths and angles corresponding to these parameters are given in Figure 4. The anisotropic temperature factors of the gold atoms along with the principal axes vectors are given in Table IV. Figure 5 shows the molecular packing. The observed and calculated structure factors are given in Table V.

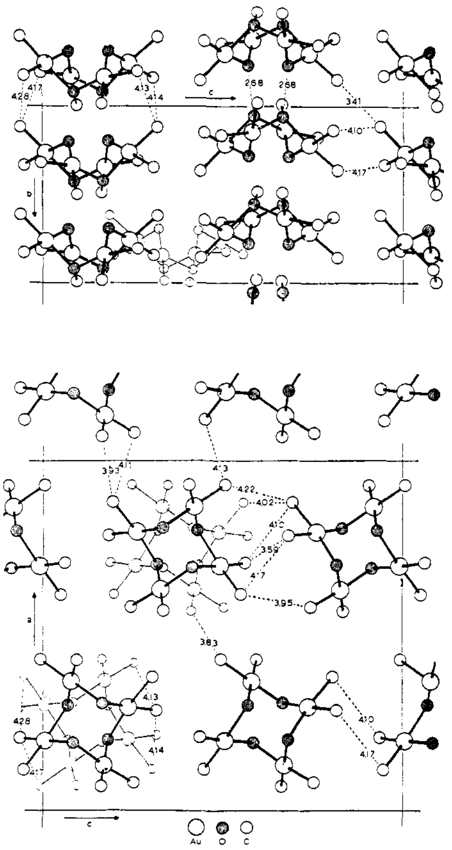

Figure 5. Projection of the structure of $[(CH_3)_2AuOH]_4$ down the a axis (above). Projection of the structure of $[(CH_3)_2AuOH]_4$ down the b axis (below). Interatomic distances are given in ångström units on both illustrations

Discussion

Dimethylgold(III) hydroxide occurs as a tetrameric molecule in the crystal with the bridging hydroxo groups and the two bound methyl groups giving the expected four-coordination of the gold(III). Consequently, the molecular structure is quite different from that suggested for the trimethylsiloxydimethylgold. There are several indications that different crystalline modifications of dimethylgold hydroxide exist, and the one studied was that obtained by slow evaporation of a benzene solution at low temperature.

The tetrameric molecule shown in Figure 4 has approximate S_4 symmetry. It does not even approxi-

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(14) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

Table IV. Final Gold Thermal Parameters[a] with Their Estimated Standard Deviations in Parentheses and the Parameters for the Ellipsoids of Vibration

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au(1)	0.00391	0.00881	0.00300	−0.00039	−0.00001	0.00053
	(0.00016)	(0.00158)	(0.00024)	(0.00026)	(0.00019)	(0.00045)
Au(2)	0.00308	0.01104	0.00416	−0.00052	0.00037	0.00080
	(0.00015)	(0.00151)	(0.00019)	(0.00032)	(0.00014)	(0.00035)
Au(3)	0.00296	0.01017	0.00458	0.00050	−0.00010	0.00121
	(0.00015)	(0.00161)	(0.00036)	(0.00029)	(0.00020)	(0.00046)
Au(4)	0.00271	0.00975	0.00465	−0.00042	0.00023	0.00043
	(0.00015)	(0.00145)	(0.00022)	(0.00030)	(0.00013)	(0.00034)

[a] The temperature factor has the form $\exp\,[-(\beta_{11}h^2 \ldots + 2\beta_{12}hk \ldots)]$.

Table V. Calculated and Observed Structure Factors

H	L	F(O)	F(C)
K=0			
0	4	642	595
0	12	927	970
0	16	204	187
1	6	373	-371
1	10	220	181
1	14	486	-481
2	0	1021	-1258
2	4	867	-761
2	6	75	27
2	8	415	-420
2	12	450	-401
2	16	181	-175
3	2	533	-479
3	6	224	176
3	10	545	565
4	0	790	-737
4	2	118	-87
4	4	741	704
4	6	92	-65
4	8	644	690
4	12	308	-287
5	2	683	690
5	4	64	75
5	6	129	106
5	10	522	-471
5	14	166	163
6	0	461	419
6	2	204	196
6	4	66	93
6	12	213	190
7	2	237	202
7	6	157	-128
7	10	358	-331
8	2	145	-127
8	4	833	-819
8	8	780	-744
8	16	140	-140
9	2	479	-407
9	6	129	97
9	10	532	554
10	0	545	501
10	2	76	-76
10	4	734	668
10	6	124	110
10	8	545	520
10	12	177	159
10	16	127	126
11	2	316	-263
11	4	155	155
11	6	212	-178
11	14	227	-235
12	0	1053	-1054
12	2	154	154
12	4	243	-206
12	12	376	-411
13	2	511	471
13	6	194	165
13	10	188	-183
13	14	221	212
14	0	519	482
14	2	99	-104
14	4	103	91
14	6	192	-196
14	12	193	186
16	0	394	356
16	6	191	173
16	12	166	169
17	2	319	-302
17	10	175	172
18	0	362	-345
18	12	159	-156
K=1			
1	3	263	240
1	4	596	517
1	5	403	-313
1	7	269	-226
1	8	448	-423
1	9	154	132
1	12	178	-208
2	2	168	-128
2	3	323	-293
2	4	117	-72
2	5	453	-399
2	6	1091	-1175
2	7	373	349
2	9	135	139
2	10	185	-158
2	15	104	-94
3	3	102	-119
3	4	597	-518
3	5	360	306
3	7	268	257
3	8	623	602
3	12	352	377
4	1	81	90
4	2	900	933
4	3	148	-106
4	6	920	917
4	10	476	501
4	14	179	208
5	1	92	-90
5	3	364	-358
5	4	552	-524
5	5	280	238
5	7	87	95
5	8	89	-73
5	9	163	-193
5	12	238	-255
6	1	145	-163
6	2	1171	-1236
6	3	403	385
6	5	374	339
6	6	141	-108
6	7	226	-213
6	9	167	-153
6	10	513	-575
6	14	297	-413
7	1	110	111
7	3	305	298
7	4	638	647
7	5	299	-292
7	7	152	-163
7	8	96	-69
7	9	109	115
7	12	125	156
8	2	583	616
8	3	157	-161
8	4	139	-144
8	5	96	-75
8	6	232	219
8	8	122	-101
8	10	189*	259
9	4	186	203
9	8	200	-237
10	0	131	141
10	2	191	162
10	3	137	-156
10	4	159	161
10	5	225	-249
10	6	449	-487
10	7	194	208
10	8	107	129
11	1	117	-110
11	3	168	-210
11	4	414	-448
11	5	173	224
11	7	134	165
12	0	215	-227
12	2	300	-363
14	2	144	180
K=2			
0	4	787	-930
0	8	464	-495
0	9	259	-273
0	11	359	-364
0	12	501	-495
0	13	303	326
0	16	211	-203
1	2	313	286
1	3	249	-227
1	5	113	106
1	6	328	330
1	9	147	-139
1	10	168	172
1	11	324	328
1	13	258	255
1	14	258	279
2	0	648*	942
2	1	147	-159
2	4	678	723
2	5	176	-164
2	8	448	478
2	12	294	315
2	16	154	152
3	1	344	367
3	2	46	9
3	3	289	-272
3	5	194	-136
3	6	214	-174
3	7	156	-148
3	9	286	-312
3	10	260	-279
3	11	204	191
3	14	158	-120
4	1	611	-644
4	2	128	112
4	3	393	-387
4	4	411	-392
4	5	202	182
4	7	235	-250
4	8	304	-335
4	9	384	420
4	11	268	286
4	13	202	-201
5	1	501	-552
5	2	233	-216
5	3	303	296
5	5	122	110
5	7	222	210
5	9	266	273
5	10	145	149
5	11	269	-272
5	13	171	-178
6	0	220*	-279
6	1	198	142
6	2	148	-138
6	3	191	160
6	4	161	-133
6	5	77	61
6	6	95	-90
6	9	87	-89
7	1	153	-149
7	3	269	274
7	6	153	122
7	9	233	233
7	10	218	196
8	1	435	420
8	2	69	72
8	3	347	309
8	4	643	621
8	5	207	-189
8	6	109	107
8	7	226	209
8	8	440	469
8	9	305	-351
8	11	216	-229
8	16	130	128
9	1	318	317
9	2	136	115
9	3	376	-338
9	5	200	-183
9	6	164	-157
9	7	247	-246
9	9	284	-317
9	10	274	-307
9	11	195	194
10	0	581	-543
10	3	239	-220
10	4	577	-570
10	8	435	-417
10	9	199	213
10	12	198	-197
11	1	220	179
11	2	165	137
11	3	128	-112
11	5	140	122
11	6	178	161
11	10	105	138
12	0	643	601
12	1	397	-403
12	3	149	-110
12	4	363	316
12	8	212	189
12	11	169	175
12	12	183	229
12	13	162	-171
13	1	348	-329
13	2	203	-161
13	3	210	188
13	6	174	-120
13	11	170	-180
14	0	316	-260
14	1	197	168
14	2	115	121
14	4	155	-146
14	6	163	133
16	1	215	203
17	1	263	232
18	0	202	186
18	1	166	-123
K=3			
1	3	220	-241
1	4	248	216
1	5	432	391
1	7	359	334
1	9	124	-124
1	13	106	-105
1	15	104	-74
1	16	149	102
2	1	50	-71
2	2	518	590
2	3	359	360
2	5	557	577
2	6	193	215
2	7	474	-501
2	9	216	-213
2	10	327	301
2	11	114	-101
2	13	189	-140
2	14	224	195
2	15	129	113
2	17	121	107
3	1	91	-13
3	3	163	137
3	4	308	-279
3	5	582	-565
3	7	466	-517
3	8	149	-133
3	9	107	76
3	12	183	-176
3	13	117*	88
3	16	228	-190
3	17	133	-113
4	1	152	-167
4	2	673	-721
4	3	112	103
4	5	198	-186
4	6	674	-669
4	7	262	259
4	10	389	-394
4	11	178	139
4	14	245	-198
5	1	209	210
5	3	514	492
5	5	197	-151
5	8	351	369
5	9	204	221
5	11	136	116
5	12	252	261
5	13	128	116
5	15	184	168
5	16	167	124
6	1	259	285
6	2	473	510
6	3	571	-601
6	5	446	-404
6	6	841	846
6	7	230	203
6	9	209	229
6	10	309	312
6	11	138	-106
6	13	169*	120
6	14	142	106
6	15	243	-220
6	17	122	-130
6	18	150	131
7	1	269	-248
7	3	491	-471
7	4	130*	92
7	5	396	393
7	7	221	200
7	8	329	-333
7	9	178	-173
7	12	213	-216
7	13	143	-141
7	15	184	-179
7	17	145*	105
8	0	150	145
8	1	82	-71
8	2	323	-338
8	3	292	283
8	4	96*	78
8	6	429	-423
8	9	118	-125
8	10	249	-204
8	15	105	102
9	3	125	-134
9	4	159	143
9	5	154	168
9	7	174	141
9	9	158	-118
9	16	100	74
10	0	189	-200
10	1	116	-90
10	2	195	162
10	3	220	227
10	4	118	-120
10	5	366	382
10	6	119	-100
10	7	294	-309
10	9	125	-85
11	1	205	184
11	3	282	302
11	4	177	-158
11	5	245	-274
11	7	205	-203
11	8	129	126
11	13	107	124
12	2	161	135
12	3	197	-194
12	5	123	-116
12	6	250	239
13	1	142	-142
13	5	128	-140
14	2	342	-329
14	5	220	-240
14	6	194	-163
14	7	219	248
14	10	166	-175
15	4	175	139
15	5	255	248
15	7	218	233
16	2	280	267
16	6	152	163
16	7	135	-133
16	10	131	137
K=4			
0	4	778	907
0	5	229	-250
0	8	858	819
0	11	196	172
0	13	240	-227
1	2	285	278
1	3	150	-130
1	5	185	-202
1	6	197	-177
1	10	518	-484
1	11	159	-159
1	13	230	-230
2	0	321*	-523
2	1	119	140
2	3	160	-145
2	4	559	-579
2	5	202	210
2	8	398	-424
2	9	216	175
2	12	230	-195
2	13	105	105
3	1	131	-134
3	2	381	391
3	3	229	220
3	5	195	187
3	6	210	185
3	7	137	137
3	9	253	254
3	11	101	-98
3	14	219	205
4	0	809	922
4	1	244	241
4	2	104	-107
4	3	283	291
4	5	101	-99
4	7	138	132
4	8	155	-152
4	9	251	-262
4	11	166	-155
4	12	369	362
5	1	287	272
5	2	485	-472
5	3	114	-107
5	9	147	-133
5	10	284	286
5	11	152	131
5	14	155	-135
6	1	66	-50
6	3	75	-52
6	4	229	199
6	6	135	134
6	8	180	167
7	2	304	-258
7	3	258	-226
7	5	166	-160
7	6	102	-98
7	7	141	-129
7	9	187	-206
7	14	143	-151
8	0	911	-949
8	1	196	-157
8	3	286	-272
8	4	222	-149
8	5	181	158
8	7	135	-119
8	9	275	280
8	11	133	154
8	12	362	-383
9	1	114	-91
9	2	464	447
9	3	305	282
9	5	248	233
9	6	210	189
9	7	221	215
9	9	282	287
9	10	111	-120
9	14	224	228
10	0	681	614
10	3	244	215
10	4	386	338
10	5	119	-123
10	8	204	199
10	9	222	-214
10	12	232	250
11	1	190	-152
11	5	125	-133
11	10	202	-204
12	1	289	257
12	4	445	-427
12	5	115	90
12	8	402	-372
13	1	213	206
13	2	248	-227
13	10	266	265
14	1	155	-140
14	2	116	-136
14	4	212	176
14	8	192	172
16	0	214	-179
17	1	149	-151
17	2	164	167
K=5			
1	3	177*	-112
1	4	629	-490
1	8	207	221
2	1	157	-164
2	2	682	-706
2	6	347	341
2	10	277	-308
2	11	208*	127
2	14	249	-286
3	1	186	189
3	3	295	272
3	4	768	616
3	7	211	224
3	8	216	-168
4	1	201	210
4	2	571	540
4	3	283	-251
4	6	301	277
4	7	189	-186
4	10	246	269
5	1	253	-279
5	3	250	-245
5	4	164	181
5	7	238	-211
5	8	315	-350
5	12	204	-209
6	1	136	-147
6	2	144	-145
6	3	287	243
6	6	1019	-866
6	7	271	230
7	1	166	175
7	4	331	-348
7	8	349	395
7	12	206	205
8	2	187	173
8	6	367	381
9	4	263	-237
10	2	254	-266
10	6	302	320
11	4	341	355
11	8	222	-224
14	2	228*	335
15	4	235	-297

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mately have the higher D_{2d} symmetry that might be expected. The eight crystallographically independent Au–C bond lengths range from 1.84 to 2.27 Å with a mean of 2.05 ± 0.08 Å (average deviation from the mean). Similarly, the Au–O bond lengths range from 1.87 to 2.40 Å with a mean of 2.15 ± 0.12 Å. There is a suggestion that both the Au–O and Au–C distances divide into two groups on the basis of length, each group being internally related by the approximate S_4 symmetry. This would lead to recognizable monomer units in the tetramer molecule. Low-temperature counter data would be required to confirm or reject this suggestion.

No reliable value for the covalent radius of square-planar gold(III) has been given. The value deduced from the chloride Au_2Cl_6[15] is 1.25 Å. Pauling[16]

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(15) E. S. Clark, D. H. Templeton, and C. H. MacGillavry, *Acta Cryst.*, 11, 284 (1958).

(16) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 224.

has suggested the value 1.40 Å for the octahedral radius of gold(IV) from data on the structure of $AuSb_2$, and with the heavy transition metals the covalent radii seem relatively insensitive to the formal oxidation state. The sums of the latter value and the covalent radii of carbon and oxygen give Au–C = 2.17 and Au–O = 2.06 Å. Comparison with the average bond lengths Au–C = 2.05 and Au–O = 2.15 Å tends to suggest that the ring bonds involving three-coordinate oxygen are relatively weaker than the gold–carbon bonds as might be expected.

The bond angles at the bridging oxygens are close to the expected tetrahedral angles, average value ∠Au–O–Au = 111°. This is in contrast to the four-membered ring in di-μ-hydroxo-bistetraamminedicobalt(III) chloride tetrahydrate[17] where the Co–O–Co angle is constrained to 100.1°. Although hydroxo-bridged transition metal complexes have been known since Werner's time,[18] this cobalt complex is apparently the only other transition metal compound with hydroxo bridges for which the detailed structure is known.[18a] The angles at the gold atoms in $(CH_3)_2AuOH$ are approximately the right angles expected for square-planar coordination. In all of the dialkylgold(III) compounds studied from the early X-ray investigations of $(C_2H_5)_2AuBr$[19] and $(C_3H_7)_2AuCN$[20] to the recent spectroscopic studies on the aquodimethylgold(III) ion,[4] square-planar coordination with *cis*-alkyl groups has always been observed. Alkyl groups are also observed always to occupy *cis* positions in the coordination sphere of square-planar platinum(II) and in the octahedral trialkylplatinum(IV) compounds. It has been suggested that this is a consequence of the *trans* effect of methyl groups.[4] The approximately 90° external angles of the $[(CH_3)_2AuOH]_4$ ring lead to quite small separations of about 2.75 Å for the two methyl groups bound to the same ring atom. The van der Waals packing radius is about 2.0 Å for a methyl group.[16] The distances between adjacent methyl groups of the same molecule bound to different ring atoms are much longer and in the range 4.5–4.7 Å.

These compact molecules pack tightly together in the crystals. The rings stack one above the other along the *b* direction to form an infinite column as may be seen in Figure 5. Two of the oxygens are directed toward oxygens of the ring below, and two point toward oxygens of the ring above with very short oxygen–oxygen distances of 2.66 and 2.68 Å. Since this distance is similar to the oxygen–oxygen distance in ice, 2.75 Å,[21] the molecules are assumed to be held together in the columns by hydrogen bonding. Similarly the cross ring oxygen–oxygen interactions of 2.73 and 2.87 Å indicate intramolecular hydrogen bonding. These suggestions are supported by the observation of a very broad band in the infrared spectrum of the solid typical of hydrogen-bonded OH groups. Within the column, the methyl–methyl contacts are in the range 4.1–4.3 Å. The molecular shape also allows very efficient packing between columns, and the many methyl–methyl contacts are in the range 3.4–4.3 Å. The standard deviations in all of these methyl–methyl contacts are approximately 0.2 Å.

The molecular weight data indicate that the molecule is also tetrameric in benzene solution. The similarity of the pmr spectra for solutions in benzene and the different solvents listed in Table I over a wide temperature range also indicates that the tetramer is present in the other solutions. Although the molecule has approximately S_4 symmetry in the crystal and this leads to a separation of the methyl groups into "axial" and "equatorial," it is surprising that this conformer persists in the solution as is indicated by the two equal intensity methyl proton resonances. Simple rotation about the Au–O bonds would take the conformation observed for the molecule in the crystal into the more symmetrical conformation where all four gold atoms lie in a plane. This has D_{2d} symmetry, and all of the eight methyls are equivalent. This rotation about the Au–O bonds might be expected to have a very low activation energy, and coalescence of the two resonance signals should therefore occur at low temperatures. In spite of this, the two signals show little broadening up to the highest temperature studied, 94°. At these temperatures, the compound decomposes to produce gold mirrors and colloidal gold. It is possible that intramolecular hydrogen bonding could hold the molecule in the less symmetrical conformation; however, this seems unlikely since the pmr spectra are very similar in such different solvents as benzene, chloroform, and dimethyl sulfoxide. The infrared spectra of the solutions also indicate that the strong hydrogen bonding present in the solid has disappeared.

Another possible explanation for the nonequivalence of the methyl groups of the dissolved molecule involves interactions between the lone electron pair on each bridging oxygen and an axial position on a gold(III). Models indicate that small rotations about the Au–O bonds in the sense opposite to that taking the molecule into the D_{2d} conformation would bring one lone pair adjacent to a gold(III) while maintaining the S_4 symmetry of the molecule. If this were carried to the extreme where all three Au–O bonds were comparable, a very compact structure similar to that suggested for the tetramer of $(CH_3)_3PtOH$[6] would be obtained. In the crystal, these Au–O interactions range from 3.34 to 3.50 Å and are too long to indicate significant bonding; however, this configuration would lead to less efficient packing in the *b* direction and weakening of the intermolecular hydrogen bonding. The best evidence for strong axial interaction is the observation that the aquo ion behaves like a triprotic acid (Figure 3). Since it is unlikely that oxo groups exist at pH 8, the doubly negative anion would be expected to have a square-pyramidal structure. There is also a considerable body of synthetic and structural evidence that such interactions may be the rule rather than the exception with gold(III). Crystals of bis(dimethylglyoximato)gold(III) dichloroaurate(I) contain essentially six-coordinate gold(III). The equatorial positions are occupied by the four nitrogen atoms of the two dimethylglyoximate ligands while

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(17) C. K. Prout, *J. Chem. Soc.*, 4429 (1962).

(18) See, *e.g.*, C. L. Rollinson in "The Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, Chapter 13.

(18a) NOTE ADDED IN PROOF. Since the completion of the manuscript, the structures of tri-μ-hydroxo-bis[triamminecobalt(III)] bromide and chloride have been reported: P. Anderson, *Acta Chem. Scand.*, 21, 243 (1967).

(19) A. Borowoy, C. S. Gibson, G. C. Hampson, and H. M. Powell, *J. Chem. Soc.*, 1690 (1937).

(20) R. F. Phillips and H. M. Powell, *Proc. Roy. Soc.* (London), A173, 147 (1939).

(21) L. E. Sutton, Ed., "Interatomic Distances," The Chemical Society, London, 1958.

the $AuCl_2^-$ anion coordinates in the axial positions with the formation of gold–gold bonds of length 3.26 Å.[22] In the compound $Cs_2Au^IAu^{III}Cl_6$, the trivalent gold is at the center of a tetragonally distorted octahedron with four gold–chlorine distances of 2.42 Å and two of 3.13 Å.[23] In AuF_3, a fluorine-bridged polymer, the gold atoms are surrounded by four fluorines in a square plane with two at 2.04 Å (bridging) and two at 1.91 Å (nonbridging). Cross linking between chains with Au–F distances of 2.69 Å completes a tetragonally distorted octahedral environment about each gold atom.[24] The structures of AuF_3 and $(CH_3)_2AuOH$, which are formally isoelectric, show many similarities. In each, a given unit is linked to two adjacent units by *cis* bridges. While the chain closes with the hydroxide to give an eight-membered ring, the fluoride structure consists of infinite helical chains. Gold(III) also forms the series of compounds with diarsine, $[Au(diars)_2](ClO_4)_3$, $[Au(diars)_2I](ClO_4)_2$, and $[Au(diars)_2I_2](ClO_4)$, in which the gold(III) is respectively four-, five-, and six-coordinate.[25] A preliminary report of an X-ray investigation of trichloro-2,2-biquinolylgold(III) indicates that this compound has a square-pyramidal structure with an axial chloride.[26]

It is interesting to compare the behavior of dimethylgold(III) with that of the dialkyl group IIIb moieties. Dimethylthallium(III) hydroxide which differs only by the presence of two more d electrons behaves quite differently. It is a strong base in aqueous solution, and the hydroxide probably has a predominantly ionic structure. In contrast, dimethylgallium(III) hydroxide is in many ways similar to the gold analog. It also exists in the crystal as a tetrameric molecule with an eight-membered ring structure.[27] In the crystal, the molecular symmetry is only C_i with an approximation to C_{2h}. There is some distortion from the expected tetrahedral coordination about the gallium atoms, and the angles within the ring are $\angle$O–Ga–O = 98.8°, $\angle$Ga–O–Ga = 133.1°. The external angles are quite large, $\angle$C–Ga–C = 129.2°, giving an average separation of the methyl groups bound to the same ring atom of about 3.5 Å, much greater than the value observed for the gold compound, 2.75 Å.

There is some question as to whether the tetrameric dimethylgallium(III) hydroxide persists in solution with organic solvents or whether depolymerization occurs.[28] Cryoscopic molecular weight measurements indicated a trimer in solution; however, considering the problems involved in determining such large molecular weights, it is possible that the smaller value was caused by experimental difficulties. Dipole moment measurements[28] gave a value of *ca.* 1.8 D; however, these measurements were only made at one temperature, a procedure which can lead to relatively large errors in the value of the permanent dipole moment.

Both trimethylsiloxydimethylgold and trimethylsiloxydimethylgallium are reported to be dimers[7,29] in contrast to the hydroxides which are both tetramers. This seems to be predominantly a steric effect, since the trimethylsiloxy group is too bulky to replace the hydroxo group in models of the dimethylgold hydroxide tetramer. Unless the Au–O bonds are much longer than in the hydroxide, the Au–Au distance in the trimethylsiloxydimethylgold will be unusually short, *ca.* 3.1 Å, compared to *ca.* 3.6 Å in the hydroxide.

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(24) F. W. B. Einstein, P. R. Rao, J. Trotter, and N. Bartlett, *J. Chem. Soc., Sect. A*, 478 (1967).

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