

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA 55455**Synthesis, Structure, and Bonding of Dimethylgold(III) Compounds. Proton Magnetic Resonance and Vibration Spectra and Normal-Coordinate Analyses of $(\text{CH}_3)_2\text{AuL}_2^z$ Ions ($L = \text{Cl}^-, \text{Br}^-, \text{OH}^-,$ and H_2O)¹**BY WILLIAM M. SCOVELL² AND R. STUART TOBIAS³

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The new organogold(III) complexes $[(\text{C}_6\text{H}_5)_4\text{As}][(\text{CH}_3)_2\text{AuX}_2]$, $\text{X}^- = \text{Cl}^-, \text{Br}^-,$ and I^- , and $\text{Cs}[(\text{CH}_3)_2\text{AuCl}_2]$ have been synthesized. All of these compounds undergo substitution reactions rapidly. Dimethyl sulfide reacts rapidly with an aqueous solution of $(\text{CH}_3)_2\text{AuNO}_3$ to yield $[(\text{CH}_3)_2\text{Au}(\text{S}(\text{CH}_3)_2)_2]\text{NO}_3$. Raman, infrared, and pmr spectra are reported for the complexes. The vibrational spectra of the complex chloride and bromide anions permit an unequivocal assignment of the *cis* structure to the complexes. In these compounds, $\nu_s(\text{AuC}_2)$ is always higher than $\nu_{as}(\text{AuC}_2)$. In order to ascertain the influence of the σ -bonded carbanion ligands on the other ligands in the first coordination sphere, normal-coordinate analyses were carried out for $(\text{CH}_3)_2\text{AuCl}_2^-$, $(\text{CH}_3)_2\text{AuBr}_2^-$, $(\text{CH}_3)_2\text{Au}(\text{OH})_2^-$, and $(\text{CH}_3)_2\text{Au}(\text{OH}_2)_2^+$ as well as for AuCl_4^- and AuBr_4^- using a Urey-Bradley force field. Trends in the vibrational frequencies and in the force constants indicate that the ligands fall generally in the same *trans*-influence sequence as found in studies of platinum(II) derivatives, *i.e.*, $(\text{CH}_3)_2\text{S} > \text{Br}^- > \text{Cl}^- > \text{en} > \text{OH}^- > \text{H}_2\text{O}$. In contrast to the isoelectronic dialkylplatinum(II) complexes, the most energetically favorable situation for the $(\text{CH}_3)_2\text{Au}^{\text{III}}$ moiety occurs when two additional ligands are bound by primarily electrostatic interactions. Replacement of two halides in the AuX_4^- anions ($\text{X}^- = \text{Cl}^-, \text{Br}^-$) by two CH_3^- groups leads to a decrease of 36 and 33%, respectively, in the Au-Cl and Au-Br stretching force constants. In these gold(III) complexes where π bonding is presumably relatively unimportant, the *trans* influence of methide is much greater than that of cyanide which is a reversal of the behavior found for platinum(II). A brief discussion is presented concerning problems associated with vibrational analyses of large inorganic complexes.

Introduction

Dialkylgold(III) halides have been known for many years since the synthesis of $(\text{C}_2\text{H}_5)_2\text{AuBr}$ by Pope and Gibson in 1907.⁴ Although initially this compound was thought to be saltlike, a cryoscopic molecular weight determination many years later showed it to be dimeric.⁵ An X-ray crystal structure determination in 1937 showed that the compound had di- μ -bromo bridges and essentially square-planar coordination about the gold(III).⁶

The di- μ -halogeno bridges of the dimethylgold(III) halides are, in general, cleaved easily by bases such as ammonia,^{4,5} pyridine,⁵ dibenzyl sulfide,⁷ mercaptides,⁸ ethylenediamine,^{5,7,9,10} 1,10 phenanthroline,¹¹ and 2,2'-bipyridyl.^{7,10,11} All of these compounds appear to contain gold(III) in a basically square-planar structure.

Some time ago, we examined the cation produced by aquation of $[(\text{CH}_3)_2\text{AuI}]_2$ in the reaction $(\text{CH}_3)_2\text{AuI}_2 + 2\text{AgNO}_3 \rightarrow 2(\text{CH}_3)_2\text{Au}(\text{OH}_2)_n^+ + 2\text{NO}_3^- + 2\text{AgI}$ and found it to have the *cis* structure.¹² Presumably two

strongly bound water molecules complete the square plane about gold, but their average lifetime appears to be no longer than *ca.* 2×10^{-5} sec.¹³ Hydrolysis in strongly alkaline solution yields a *cis* anionic species, presumably $(\text{CH}_3)_2\text{Au}(\text{OH})_2^-$.¹²

In this communication, we report the syntheses of several new ionic compounds containing organogold species of the type $(\text{CH}_3)_2\text{AuL}_2^z$, $z = \pm 1$. Vibrational spectroscopy has been used to study the effect of the σ -bonded alkyl groups on the other ligands, L, in the first coordination sphere of the transition metal.

Experimental Section

General Data.—The starting material for the preparation of the organogold compounds, di- μ -iodo-tetramethyldigold(III), was synthesized by the method of Brain and Gibson⁷ with yields of 35–40%. The other halides, di- μ -bromo-tetramethyldigold(III) and di- μ -chloro-tetramethyldigold(III), were synthesized as described elsewhere.¹⁴ Tetraphenylarsonium bromide was prepared by dissolving $(\text{C}_6\text{H}_5)_4\text{AsCl}$ (0.2 mol) in hot distilled water and adding NaBr (0.3 mol) dissolved in a minimum amount of water. The $(\text{C}_6\text{H}_5)_4\text{AsBr}$ which precipitated as needlelike crystals upon cooling was collected on a frit and dried.

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory and by the Clark Microanalytical Laboratory.

Tetraphenylarsonium Dichlorodimethylaurate(III) and Tetraphenylarsonium Dibromodimethylaurate(III), $[(\text{C}_6\text{H}_5)_4\text{As}][(\text{CH}_3)_2\text{AuX}_2]$, $\text{X}^- = \text{Cl}^-, \text{Br}^-$.—Tetraphenylarsonium chloride or bromide (1.1×10^{-3} mol) was dissolved in 30 ml of benzene-methanol solution. To this solution was added 30 ml of a benzene solution of $[(\text{CH}_3)_2\text{AuX}]_2$ (1.07×10^{-3} mol) dropwise with stirring at *ca.* 40°. The resulting clear, colorless solution was evaporated to *ca.* 40 ml and cooled to 5°, and the white crystals which precipitated were collected on a filter and dried; yield 90%. *Anal.* Calcd for $\text{C}_{26}\text{H}_{26}\text{AsAuCl}_2$: C, 45.8; H, 3.83; Cl, 10.4.

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(2) Taken from a thesis submitted by W. M. S. to the Graduate School of the University of Minnesota for the Ph.D. degree, 1969.

(3) Department of Chemistry, Purdue University, Lafayette, Ind. 47907.

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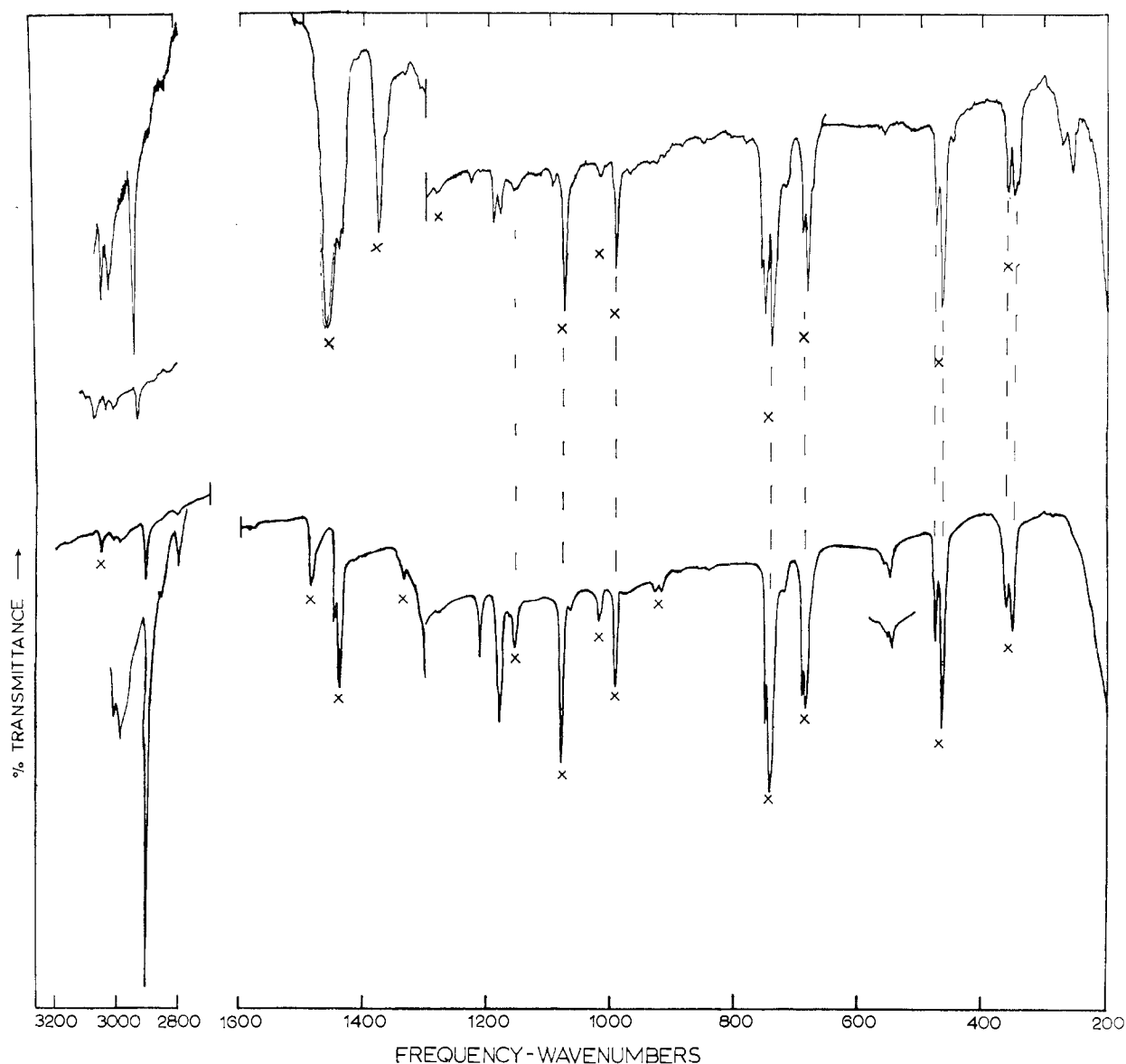


Figure 1.—Infrared spectra of $[(C_6H_5)_4As][(CH_3)_2AuX_2]$, $X^- = Cl^-$ (top) and Br^- (bottom). The bands due to $(C_6H_5)_4As^+$ are marked with X.

Found: C, 45.5; H, 3.99; Cl, 9.83; mp 157° . Calcd for $C_{26}H_{26}AsAuBr_2$: C, 40.6; H, 3.40; Au, 25.6; Br, 20.8. Found: C, 41.3; H, 3.65; Au, 25.8; Br, 21.1; mp 153° dec.

Cesium Dichlorodimethylaurate(III), $Cs[(CH_3)_2AuCl_2]$.—Dimethylgold(III) hydroxide¹² (0.3 g, 1.2×10^{-3} mol) was added to 40 ml of methanol at 0° . Sufficient 0.2 M HCl was added (12.5 ml, 2.5×10^{-3} mol) to dissolve the hydroxide completely. The excess acid was neutralized by dropwise addition of an aqueous solution of Cs_2CO_3 (1.3×10^{-3} mol). The solution was evaporated to dryness. Alternatively, $[(CH_3)_2AuOH]_4$ was dissolved in a solution of HCl in ethanol, and CsCl (1.3×10^{-3} mol) was added. The solution was evaporated to ca. 3 ml at which point the white crystalline product formed; yield 80%. *Anal.* Calcd for $C_2H_6CsAuCl_2$: C, 5.57; H, 1.39; Cl, 16.5. Found: C, 4.81; H, 1.36; Cl, 16.6.

Tetraphenylarsonium Diiododimethylaurate(III), $[(C_6H_5)_4As][(CH_3)_2AuI_2]$.—Dimethylgold(III) hydroxide (0.244 g, 1×10^{-3} mol) was dissolved in a minimum amount of ethanol containing 12 ml of 0.2 M HI (2.4×10^{-3} mol). An ethanol solution of $(C_6H_5)_4AsCl$ (0.460 g, 1.1×10^{-3} mol) was added dropwise yielding a light yellow precipitate which was collected on a frit and dried; yield 47%. The purity was checked by pmr spectroscopy.

Bis(dimethyl sulfide)dimethylgold(III) Nitrate, $[(CH_3)_2Au(S(CH_3)_2)_2]NO_3$.—Dimethylgold(III) hydroxide (2.02 g, 8.3×10^{-3} mol) was dissolved in 5 ml of 2 M nitric acid (1×10^{-2} mol). At ca. 2° , $(CH_3)_2S$ (3 g, 4.8×10^{-2} mol) was added dropwise. The two immiscible layers were stirred for 1 hr producing the reaction $(CH_3)_2Au(aq)^+ + 2(CH_3)_2S(l) = (CH_3)_2Au(S(CH_3)_2)_2(aq)^+$. The small amount of excess dimethyl sulfide was evaporated away in a stream of nitrogen. The compound was not isolated from solution.

Diamminedimethylgold(III) Chloride, $[(CH_3)_2Au(NH_3)_2]Cl$.—Dimethylgold(III) chloride (0.5 g, 1.9×10^{-3} mol) was dissolved in petroleum ether (bp $60-68^\circ$). Ammonia gas was bubbled into the solution giving a quantitative yield, presumably, of $(CH_3)_2AuNH_3Cl$. Dry ammonia gas was condensed onto the monoamine complex using a Dry Ice-2-propanol bath, and this yielded a clear, colorless solution of $[(CH_3)_2Au(NH_3)_2]Cl$. Upon slow evaporation of the excess ammonia, a white product resulted. The compound is unstable and loses ammonia very easily.

Raman Spectra.—Raman spectra were obtained using three different spectrophotometers. Initially, a standard mercury-arc Cary 81 instrument was employed. The 4358-Å mercury line was isolated using a filter solution containing 40 g of Cysorb

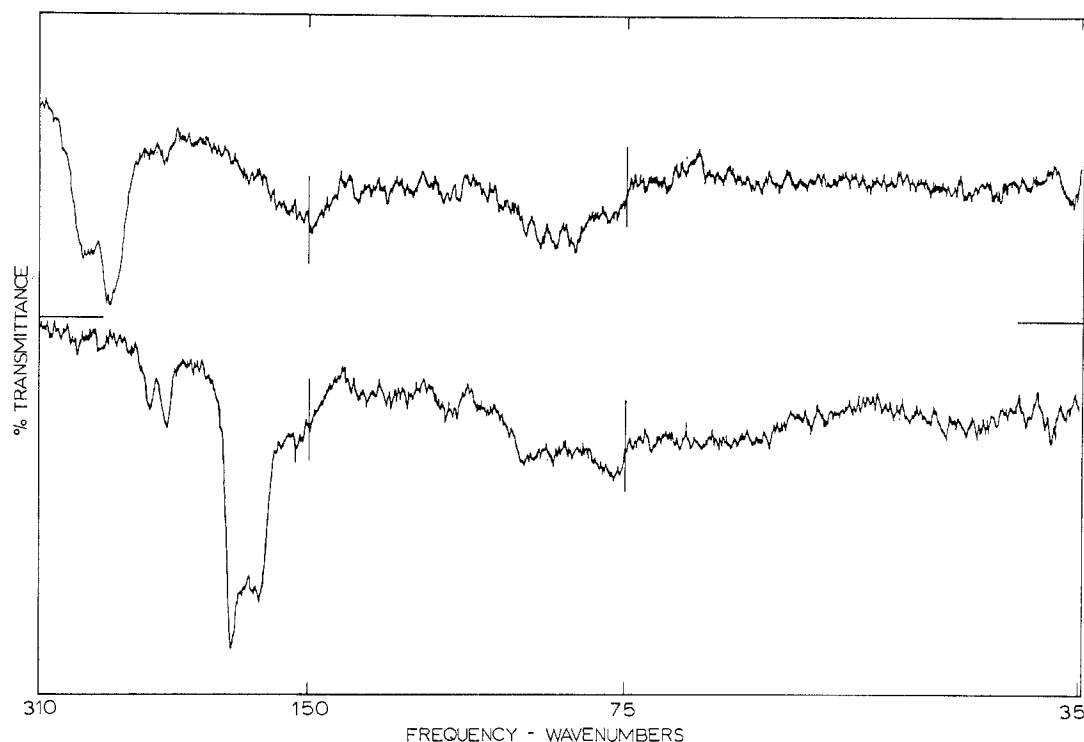


Figure 2.—Far-infrared spectra of $[(C_6H_5)_4As][(CH_3)_2AuX_2]$, $X^- = Cl^-$ (top) and Br^- (bottom). The weak bands at *ca.* 240 cm^{-1} are assigned to the cation.

UV-24 and 2 g of ethyl violet dissolved per gal of 2-propanol. Additional spectra were obtained with a laser 81^{16} using He-Ne excitation (6328 \AA). The third instrument, the Minnesota Mark I (MMI), employs a Spectra Physics Model 112 He-Ne laser (6328 \AA) producing in excess of 30 mW CW with a multi-phase wavefront. This was chopped at 600 Hz. A Spex Model 1400 double monochromator was used to disperse the spectrum. The signal from a cooled (-85°) EMI 9558A photomultiplier was detected with a Princeton Applied Research CR-4 preamplifier and a JB-4 lock-in amplifier and displayed on a Brown Honeywell recorder. This instrument was calibrated with benzene, carbon tetrachloride, and indene.

The solution spectra obtained with the Cary 81 and Hg arc excitation were taken with a 19-in., 7-mm diameter water-jacketed cell. Powder spectra were taken either with conical glass cells (Hg arc excitation) or by 90° illumination of a thin layer of powder (laser excitation). Frequencies for sharp lines are believed to be accurate to $\pm 2\text{ cm}^{-1}$.

Infrared Spectra.—Infrared spectra were recorded either on a Perkin-Elmer 521 or a Beckman IR 12 spectrometer. Spectra of solids were obtained both as KBr disks and as mulls in Halocarbon oil ($4000\text{--}1300\text{ cm}^{-1}$) and Nujol ($1300\text{--}200\text{ cm}^{-1}$). Instrument calibration was effected with polystyrene film and neat indene. Far-infrared spectra were run on a Beckman IR-11 spectrometer as Nujol suspensions between polyethylene windows.¹⁶ The frequencies of sharp bands are accurate to within $\pm 2\text{ cm}^{-1}$, while those for broad bands are within $\pm 5\text{ cm}^{-1}$.

Proton Magnetic Resonance Spectra.—Spectra were recorded with Varian A-60, A-60D, and T-60 spectrometers with the sample temperatures being approximately 35 , 40 , and 41° , respectively. Coupling constants were measured using side bands and are believed to be accurate to $\pm 0.5\text{ Hz}$.

Data and Results

Assignment of the Spectra of the Solid Complexes.—

(15) These spectra were recorded at the University of Maryland during the 1968 Laser Raman Institute and Workshop for which we thank Professor Ellis R. Lippincott.

(16) We are indebted to Professor H. P. Fritz of the Technische Hochschule München for these spectra.

TABLE I
OBSERVED FREQUENCIES OF THE *cis*-(CH_3) $_2$ AuCl $_2^-$
AND *cis*-(CH_3) $_2$ AuBr $_2^-$ IONS

[(C_6H_5) $_4$ As]- [(CH_3) $_2$ AuCl $_2$]		[(C_6H_5) $_4$ As][(CH_3) $_2$ AuBr $_2$]		Assignment
Ir a	Raman a,c	Ir a	Raman a,c	
3017 m		3015 w		$\nu_{as}(CH_3)$
2995 m		2992 w		
2911 s		2938 sh		$\nu_s(CH_3)$
2898 m		2909 m		
2809 w		2808 w		$2\delta_{as}(CH_3)$
1417 sh				$\delta_{as}(CH_3)$
1225 w		1214 m	1218 w	$\delta_s(CH_3)$
1194 m		1182 s	1188 m	
809				$\rho_r(Au-CH_3)$
	572	560 w	558 vs	$\nu_s(Au-C_2)$
563		552 m		$\nu_{as}(Au-C_2)$
281				$\nu_s(Au-Cl_2)$
	272		279 m	$\delta(C-Au-C)$
268				$\nu_{as}(Au-Cl_2)$
		197 vs	193 vs	$\nu_s(Au-Br_2)$
		179 s		$\nu_{as}(Au-Br_2)$

^a Frequencies due to $(C_6H_5)_4As^+$ have not been tabulated.

^b Spectrum obtained using both Hg and He-Ne excitation. Fluorescence occurred with the Hg arc and limited measurements to $\Delta = 200\text{--}600\text{ cm}^{-1}$. With the laser excitation, the background was even more intense. ^c The C-H stretching region is partially obscured by a very intense Lyman ghost characteristic of the 1200-groove/mm Bausch and Lomb gratings used in the Spex monochromator.

The complete Raman and infrared spectra for the complex anions $(CH_3)_2AuCl_2^-$ and $(CH_3)_2AuBr_2^-$ are tabulated in Table I. The infrared spectra of the dichloro and dibromo complexes are illustrated in Figures 1 and 2, and the laser Raman spectrum of the dibromo complex is illustrated in Figure 3. In general, the assignments of most of the frequencies were straightforward and

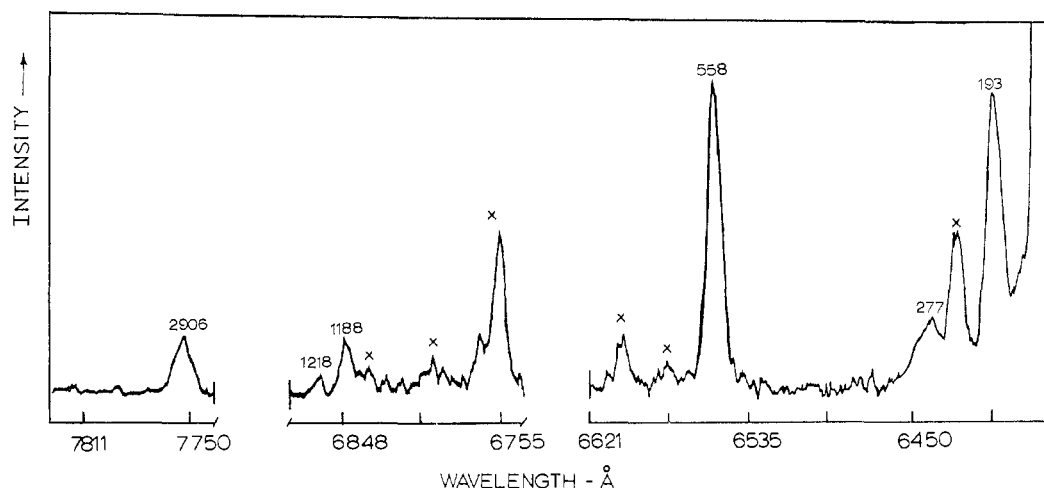


Figure 3.—Laser Raman spectrum of $[(C_6H_5)_4As][(CH_3)_2AuBr_2]$ run as a crystalline powder.

made by analogy with the aquo cation.¹² Vibrations of the cation $(C_6H_5)_4As^+$ were identified from Raman and infrared spectra of $(C_6H_5)_4AsCl$ and $(C_6H_5)_4AsBr$. The gold-halogen stretching frequencies in the *cis*- $(CH_3)_2AuX_2^-$ ions occur at considerably lower values than the corresponding stretching frequencies of the AuX_4^{17-21} anions or of the *trans*- $Au(CN)_2X_2^-$ anions.^{22,23} The Au-Br stretching vibrations are observed in both the Raman and infrared spectra, while the Au-Cl stretching vibrations either have too low an intensity to be observed in the Raman or are masked by the very intense (C-Au-C) deformation at 272 cm^{-1} . The calculated ratio of the stretching frequencies $\nu_{av}(Au-Br)/\nu_{av}(Au-Cl)$ is 0.69. This supports the assignments, since this ratio is usually *ca.* 0.70 for complex anions²⁴ and has the value 0.70 for the AuX_4^- ions and 0.71 for the *trans*- $Au(CN)_2X_2^-$ species. This value infers that the force constant for gold-chloride bonds is about 10% larger than for gold-bromide bonds in all of these compounds.

The appearance of two Raman- and infrared-active vibrations in the symmetric methyl deformation region indicates that the complexes all have the *cis* structure.¹² This structure assignment is confirmed for the $(CH_3)_2AuX_2^-$, $X^- = Cl^-$ and Br^- , anions by the observation of both symmetric and asymmetric Au- X_2 stretching frequencies in the far-infrared spectra.

Although dimethyl sulfide is not soluble in water, it is extracted into an aqueous solution containing the dimethylgold(III) aquo cation in much the same way that it reacts with the methylmercury(II) cation.²⁵ The Raman frequencies for the complex are listed in Table II. Assignments were made by comparison with the spectra of solutions of $[CH_3HgS(CH_3)_2]NO_3$ ²⁵ and

the spectrum of dimethyl sulfide.²⁶ The solutions do not exhibit the polarized band at 408 cm^{-1} observed with aqueous solutions of dimethylgold(III) nitrate and assigned to Au-O stretching involving bonds to coordinated water molecules. Of interest is the fact that the asymmetric and symmetric C-S stretches have almost the same values in the complex, 740 and 687 cm^{-1} , as observed for neat dimethyl sulfide, 742 and 691 cm^{-1} .²⁶ For the methylmercury(II) complex, these frequencies are 13 and 16 cm^{-1} lower than for the free ligand. Sulfur appears to be a much poorer ligand for dimethylgold(III) than for methylmercury(II), and, indeed, in the absence of excess dimethyl sulfide the gold complex dissociates slowly giving a Raman spectrum characteristic of the aquo cation.²⁷

TABLE II
RAMAN FREQUENCIES OF A 1.3 M AQUEOUS SOLUTION OF $[(CH_3)_2Au(S(CH_3)_2)]NO_3^a$

$\Delta\nu, \text{cm}^{-1}$	Assignment	$\Delta\nu, \text{cm}^{-1}$	Assignment
3058 m	$\nu(CH_3)$ (S- CH_3)	740 w	$\nu_{as}(C-S)$
3014 m	$\nu_{as}(CH_3)$ (Au- CH_3)	687 m	$\nu_s(C-S)$
2935 m	$\nu_s(CH_3)$ (Au- CH_3)	555 vvs	$\nu(Au-C_2)$
1237 w	$\delta_s(CH_3)$ (Au- CH_3)	293 m	$\delta(SC_2), \nu(Au-S_2)$
1202 m		266 m	$\delta(C-Au-C)$
1050 m	$\nu_1(NO_3^-)$	165 s, b	$\delta_{wag}(SC_2)$

^a Spectra recorded at *ca.* 3°.

Data illustrating trends in the gold-carbon and gold-ligand stretching frequencies and also in the methyl deformation frequencies are collected in Table III. In all of these compounds, the symmetric stretch was higher in frequency than the asymmetric stretch.

Proton magnetic resonance data for the complex cations and anions are collected in Table IV. All compounds exhibited only one methyl-gold resonance confirming their purity. The 2:1 intensity ratio of the protons of dimethyl sulfide to the dimethylgold(II) protons confirms the formation of the bis complex.

Normal-Coordinate Calculations.—In order to evaluate trends in the bonding in the $(CH_3)_2AuL_2^z$ ($z =$

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TABLE III
SKELETAL STRETCHING AND SYMMETRIC METHYL
DEFORMATION FREQUENCIES FOR COMPLEX
DIMETHYLGOLD(III) IONS

Ion	$\nu(\text{Au-C}), \text{cm}^{-1}$		$\delta_s(\text{CH}_3) (\text{Au-CH}_3), \text{cm}^{-1}$
	Raman	Ir	
$(\text{CH}_3)_2\text{Au}(\text{OH}_2)_2^{+13}$	591	...	1258, 1222
$(\text{CH}_3)_2\text{Au}(\text{OH})_2^{-13}$	586	...	1249, 1220
$(\text{CH}_3)_2\text{Au}(\text{en})^{+13}$	580	570	1245, 1220
$(\text{CH}_3)_2\text{AuCl}_2^-$	572	563	1225, 1194 ^a
$(\text{CH}_3)_2\text{AuBr}_2^-$	558	{ 560 552	{ 1218, 1188 ^a 1214, 1182 ^a
$(\text{CH}_3)_2\text{Au}(\text{S}(\text{CH}_3)_2)_2^+$	555	...	1237, 1202

^a $\delta_s(\text{CH}_3)$ taken from the ir spectrum.

TABLE IV
PROTON MAGNETIC RESONANCE DATA ON
DIMETHYLGOLD(III) COMPLEXES^a

Compound	Solvent	$\tau(\text{CH}_3), \text{ppm}$	Rel $J(^{13}\text{C-H}), \text{Hz}$	
			intens	Hz
$[(\text{C}_6\text{H}_5)_4\text{As}][(\text{CH}_3)_2\text{AuCl}_2]$	CHCl_3	8.90 ^b	...	139
$[(\text{C}_6\text{H}_5)_4\text{As}][(\text{CH}_3)_2\text{AuBr}_2]$	CHCl_3	8.79 ^b	...	139
$[(\text{C}_6\text{H}_5)_4\text{As}][(\text{CH}_3)_2\text{AuI}_2]$	CHCl_3	8.55 ^b
$[(\text{CH}_3)_2\text{Au}(\text{S}(\text{CH}_3)_2)_2]\text{NO}_3$	H_2O	8.72 ^c ($\text{CH}_3\text{-Au}$)	1	140.5
		7.43 ^c ($\text{CH}_3\text{-S}$)	2	...

^a Temperature 40°. ^b $\tau = 10$, tetramethylsilane. ^c $\tau = 10$, trimethylsilyl propanesulfonate.

± 1) ions and to compare them with the AuX_4^- anions, normal-coordinate calculations were carried out on the following dimethylgold(III) complexes: $(\text{CH}_3)_2\text{AuCl}_2^-$, $(\text{CH}_3)_2\text{AuBr}_2^-$, $(\text{CH}_3)_2\text{Au}(\text{OH})_2^-$, and $(\text{CH}_3)_2\text{Au}(\text{OH}_2)_2^+$. For comparison, calculations were also made for AuCl_4^- and AuBr_4^- which have been studied by several different workers.^{18-21,28}

The representation for the normal vibrations of an 11-atom $[(\text{CH}_3)_2\text{AuL}_2]$ structure, taking the symmetry as C_{2v} , is $\Gamma_{\text{vib}} = 9 \text{A}_1 + 5 \text{A}_2 + 5 \text{B}_1 + 8 \text{B}_2$. Only the in-plane A_1 and B_2 vibrations, *i.e.*, vibrations symmetric with respect to the plane defined by the two C, Au, and two L atoms, which are both infrared and Raman active, were considered. The molecular model used in the calculations is shown in Figure 4 which also illustrates the 26 internal coordinates used to describe the in-plane vibrations. Table V lists the molecular

TABLE V

MOLECULAR PARAMETERS FOR THE COMPLEX GOLD(III) IONS

$d(\text{Au-C}) = 2.05 \text{ \AA}^{29}$
$d(\text{Au-Cl}) = 2.42 \text{ \AA}^{30}$
$d(\text{Au-Br}) = 2.57 \text{ \AA}^{31}$
$d(\text{Au-O}) = 2.15 \text{ \AA}^{29}$
$d(\text{C-H}) = 1.09 \text{ \AA}^{32}$
$\angle(\text{H-C-H}) = (\text{H-C-Au}) = 109^\circ 28'$
$\angle(\text{L-Au-L}) = (\text{L-Au-C}) = (\text{C-Au-C}) = 90^\circ$

parameters²⁹⁻³² used in constructing the G matrices. In the calculations, the hydroxo and aquo groups were taken as single masses of 17 and 18 amu, respectively.

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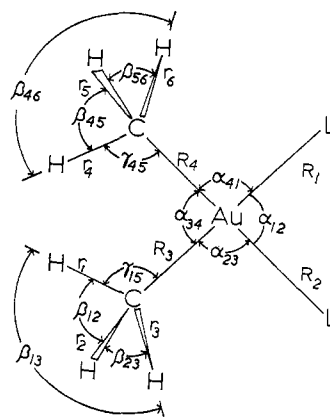


Figure 4.—Molecular model showing the internal coordinates used in the normal-coordinate calculations for the $(\text{CH}_3)_2\text{AuL}_2^{\pm}$ ions.

Because of the complexity of these ions, it was necessary to employ a simple model force field, and for this the Urey-Bradley force field (UBFF) was selected. In terms of the internal coordinates for the in-plane motion, the potential energy for these $(\text{CH}_3)_2\text{AuL}_2^{\pm}$ ions is given by

$$\begin{aligned}
 2V = & \sum_{i=1}^2 [2K'_{\text{Au-L}} R_{\text{Au-L}} (\Delta R^i_{\text{Au-L}})^2 + K_{\text{Au-L}} (\Delta R^i_{\text{Au-L}})^2] + \\
 & \sum_{i=1}^2 [2K'_{\text{Au-C}} R_{\text{Au-C}} (\Delta R^i_{\text{Au-C}})^2 + K_{\text{Au-C}} (\Delta R^i_{\text{Au-C}})^2] + \\
 & \sum_{i=1}^6 [2K'_{\text{C-H}} r_{\text{C-H}} (\Delta r^i_{\text{C-H}})^2 + K_{\text{C-H}} (\Delta r^i_{\text{C-H}})^2] + \\
 & [2H'_{\text{LAuL}} (\Delta \alpha_{\text{LAuL}})^2 + H_{\text{LAuL}} (\Delta \alpha_{\text{LAuL}})^2] + [2H'_{\text{CAuC}} (\Delta \alpha_{\text{CAuC}})^2 + \\
 & H_{\text{CAuC}} (\Delta \alpha_{\text{CAuC}})^2] + \sum_{i=1}^2 [2H'_{\text{CAuL}} (\Delta \alpha^i_{\text{CAuL}})^2 + H_{\text{CAuL}} (\Delta \alpha^i_{\text{CAuL}})^2] + \\
 & \sum_{i=1}^6 [2H'_{\text{HCH}} (\Delta \alpha^i_{\text{HCH}})^2 + H_{\text{HCH}} (\Delta \alpha^i_{\text{HCH}})^2] + \\
 & \sum_{i=1}^6 [2H'_{\text{HCAu}} (\Delta \alpha^i_{\text{HCAu}})^2 + H_{\text{HCAu}} (\Delta \alpha^i_{\text{HCAu}})^2] + \\
 & \sum_{i=1}^6 [2F'_{\text{HHQH}} (\Delta q^i_{\text{HH}})^2 + F_{\text{HH}} (\Delta q^i_{\text{HH}})^2] + \\
 & \sum_{i=1}^6 [2F'_{\text{AuHQ}} (\Delta q^i_{\text{AuH}})^2 + F_{\text{AuH}} (\Delta q^i_{\text{AuH}})^2] + \\
 & [2F'_{\text{CCQC}} (\Delta q_{\text{CC}})^2 + F_{\text{CC}} (\Delta q_{\text{CC}})^2] + \\
 & \sum_{i=1}^2 [2F'_{\text{CLQC}} (\Delta q^i_{\text{CL}})^2 + F_{\text{CL}} (\Delta q^i_{\text{CL}})^2] + \\
 & [2F'_{\text{LLQL}} (\Delta q_{\text{LL}})^2 + F_{\text{LL}} (\Delta q_{\text{LL}})^2] \quad (1)
 \end{aligned}$$

After elimination of the nonbonded distances q_{HH} , q_{AuH} , q_{CC} , q_{CL} , and q_{LL} , the potential energy expression contains all of the quadratic force constants in (1), the linear constants F' , and the internal tension constant resulting from the redundancies in the angles about the carbon atoms. As is conventional, the linear terms were taken as -0.1 of the quadratic terms. The internal tension was set equal to zero. Harmonic vibrations were assumed.

Calculations were made in a similar manner for AuCl_4^- and AuBr_4^- . Again only the in-plane ($\text{A}_{1g} + \text{B}_{1g} + \text{B}_{2g} + 2 \text{E}_u$) vibrations were considered. Values for the nonbonded $\text{X} \cdots \text{X}$ interactions, F_{XX} , were esti-

mated from Lennard-Jones 6-12 potentials for inert gases.³³ The initial values of $K(\text{Au-X})$ and $H(\text{X-Au-X})$ were taken from the article by Sabatini, *et al.*¹⁸ The trial values of the three force constants were adjusted to minimize the sum of the squares of the residuals in the frequency parameters.³⁴ Weights were taken proportional to $1/\lambda$. The calculations were carried out using standard computer programs,^{35,36} the University of Minnesota's CDC-6600, and Purdue University's CDC-6500 computers.

As has been noted earlier,¹⁹ the UBFF does not provide a very good representation of the forces operating in these AuX_4^- anions. This can be seen from the frequency fits listed in Table VII where the average error for AuCl_4^- is 7.7% and that for AuBr_4^- is 4.8%. The fit can be improved greatly by the use of a general valence force field (GVFF) employing *cis* and *trans* stretch-stretch and bend-bend interactions,^{18,28} but this requires the determination of six force constants from five in-plane frequencies. Table VI lists the

TABLE VI
UREY-BRADLEY FORCE CONSTANTS AND
STANDARD ERRORS FOR AuX_4^- IONS

Force constant ^a	AuCl_4^-	AuBr_4^-
$K(\text{Au-X})$	1.97 (0.26)	1.63 (0.11)
$H(\text{X-Au-X})$	0.57 (0.91)	0.21 (0.53)
$F(\text{X}\cdots\text{X})$	0.18 (0.28)	0.20 (0.14)

^a K and F in $\text{mdyn}/\text{\AA}$; H in $\text{mdyn } \text{\AA}/\text{radian}^2$.

TABLE VII
OBSERVED AND CALCULATED FREQUENCIES
FOR THE AuX_4^- ANIONS

	AuCl_4^-		AuBr_4^-	
	Obsd ^a	Calcd	Obsd ^a	Calcd
A_{1g}	347	334	212	208
B_{1g}	324	305	196	184
B_{2g}	171	193	102	110
E_u	356	168	252	257
E_u	173	153	100	94
	Av error	7.73%	Av error	4.77%

^a Observed frequencies from ref 18.

values of the force constants obtained from the last cycle of least-squares refinement, which differ slightly from previous values because of the refinement procedure, and Table VII gives a comparison of the calculated and observed frequencies. Insofar as stretching force constants are concerned, the simple UBFF gives reliable values. The diagonal elements of the F matrix for AuCl_4^- and AuBr_4^- , 2.15 (0.29) and 1.82 (0.13) $\text{mdyn}/\text{\AA}$, may be compared with the values of Jones²⁸ obtained with a five-parameter GVFF, 2.15 and 1.80 $\text{mdyn}/\text{\AA}$.

For the $(\text{CH}_3)_2\text{AuX}_2^-$ ions, the trial values of $K(\text{Au-C})$, $K(\text{C-H})$, $H(\text{H-C-H})$, $J(\text{H-C-Au})$, $F(\text{H}\cdots\text{H})$, and $F(\text{Au}\cdots\text{H})$ were estimated from the calculation of $(\text{CH}_3)_2\text{Hg}$.³⁷ For the gold-halogen stretching force constants, 60% of the value for the corresponding AuX_4^- ion

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listed in Table VI was used. The halogen-halogen nonbonded force constants were taken from the AuX_4^- calculations. For the $H(\text{X-Au-X})$ bending constant, 60% of the AuX_4^- value was taken arbitrarily. The trial value for $H(\text{C-Au-C})$ was taken as $H(\text{X-Au-X})$ of AuCl_4^- . The value of $H(\text{C-Au-X})$ was taken as the mean of $H(\text{C-Au-C})$ and $H(\text{X-Au-X})$. Values for the $F(\text{C}\cdots\text{C})$ and $F(\text{C}\cdots\text{X})$ nonbonded constants were estimated from Lennard-Jones 6-12 potentials.³⁴ Since the only bending frequency which was observed was $\delta(\text{C-Au-C})$, the values for $H(\text{X-Au-C})$ and $H(\text{X-Au-X})$ were constrained. The particular values chosen had little effect on any of the force constants calculated except $H(\text{C-Au-C})$. No physical significance should be attached to any of the skeletal bending force constants.

It was found that interaction effects are minimal in the $(\text{CH}_3)_2\text{AuX}_2^-$ ions ($\text{X}^- = \text{Cl}^-, \text{Br}^-$), as might be expected because of the 90° skeletal bond angles and the heavy gold atom, so the UBFF was quite adequate. Since fewer frequencies were available for the two species found in aqueous solution $(\text{CH}_3)_2\text{Au}(\text{OH})_2^-$ and $(\text{CH}_3)_2\text{Au}(\text{OH}_2)_2^+$, a somewhat simplified force field was used for these two ions taking values from the $(\text{CH}_3)_2\text{AuCl}_2^-$ calculation.

The force constants from the last cycle of least-squares refinement of the $(\text{CH}_3)_2\text{AuL}_2^z$ species are listed in Table VIII, and the calculated and observed

TABLE VIII
UREY-BRADLEY FORCE CONSTANTS AND
STANDARD ERRORS FOR THE $(\text{CH}_3)_2\text{AuL}_2^z$ IONS

Force constant ^a	$(\text{CH}_3)_2\text{AuCl}_2^-$	$(\text{CH}_3)_2\text{AuBr}_2^-$	$(\text{CH}_3)_2\text{Au}(\text{OH})_2^-$	$(\text{CH}_3)_2\text{Au}(\text{OH}_2)_2^+$
$K(\text{Au-L})$	1.26 (0.08)	1.11 (0.15)	1.82 (0.07)	1.62 (0.08)
$K(\text{Au-C})$	1.51 (0.06)	1.40 (0.09)	1.71 (0.07)	1.76 (0.09)
$K(\text{C-H})$	4.62 (0.03)	4.60 (0.04)	4.61 (0.05)	4.65 (0.06)
$H(\text{L-Au-L})$	0.34 ^b	0.12 ^b	0.20 ^b	0.20 ^b
$H(\text{L-Au-C})$	0.73 ^b	0.60 ^b	0.54 ^b	0.54 ^b
$H(\text{C-Au-C})$	0.88 (0.14)	1.05 (0.18)	1.12 (0.14)	1.22 (0.17)
$H(\text{H-C-H})$	0.51 (0.01)	0.47 (0.02)	0.53 (0.02)	0.54 (0.02)
$H(\text{H-C-Au})$	0.05 (0.01)	0.05 ^b	0.05 ^b	0.05 ^b
$F(\text{Au}\cdots\text{H})$	0.50 ^b	0.50 ^b	0.50 ^b	0.50 ^b
$F(\text{H}\cdots\text{H})$	0.02 (0.02)	0.05 (0.02)	0.04 (0.03)	0.04 (0.03)
$F(\text{C}\cdots\text{C})$	0.05 ^b	0.05 ^b	0 ^b	0 ^b
$F(\text{L}\cdots\text{L})$	0.18 ^b	0.20 ^b	0 ^b	0 ^b
$F(\text{L}\cdots\text{C})$	0.08 ^b	0.08 ^b	0 ^b	0 ^b
	0 ^b	0 ^b	0 ^b	0 ^b

^a Stretching force constants in $\text{mdyn}/\text{\AA}$; bending force constants in $\text{mdyn } \text{\AA}/\text{radian}^2$. ^b Force constant constrained.

TABLE IX
OBSERVED AND CALCULATED FREQUENCIES OF $(\text{CH}_3)_2\text{AuL}_2$ IONS

$(\text{CH}_3)_2\text{AuCl}_2^-$		$(\text{CH}_3)_2\text{AuBr}_2^-$		$(\text{CH}_3)_2\text{Au}(\text{OH})_2^-$		$(\text{CH}_3)_2\text{Au}(\text{OH}_2)_2^+$	
Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
3017	3007	3015	3004	0	3005	0	3017
2911	2904	2909	2923	2914	2914	2926	2926
1417	1415	0	1387	0	1453	0	1463
1225	1214	1214	1198	1249	1234	1258	1240
809	809	0	806	0	809	0	811
572	570	558	558	586	586	591	591
281	284	279	279	441	441	406	406
272	272	197	192	267	267	275	275
0	150	0	97	0	168	0	136
2995	3006	2992	3003	3004	3004	3016	3016
2898	2904	2938	2923	0	2914	0	2926
1417	1414	0	1386	0	1452	0	1463
1194	1213	1182	1197	1220	1234	1223	1240
809	802	0	797	0	801	0	802
563	565	552	552	586	586	591	591
268	265	179	184	441	441	406	406
0	188	0	156	0	168	0	166
av. error	0.52%	av. error	0.86%	av. error	0.26%	av. error	0.32%

TABLE X
 PER CENT POTENTIAL ENERGY FOR THE $(\text{CH}_3)_2\text{AuCl}_2^-$ ANION USING A UBFF

	Obsd freq, cm^{-1}															
	A ₁								B ₂							
	3017	2911	1417	1125	809	572	281	272	2995	2898	1417	1197	809	563	268	
$K(\text{Au}-\text{Cl})$	0	0	0	0	0	0	80	6	0	0	0	0	0	0	99	
$K(\text{Au}-\text{C})$	0	0	0	1	0	63	0	0	0	0	0	1	0	64	0	
$K(\text{C}-\text{H})$	96	95	1	1	1	1	0	0	96	95	1	1	1	1	0	
$H(\text{Cl}-\text{Au}-\text{Cl})$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
$H(\text{Cl}-\text{Au}-\text{C})$	0	0	0	0	1	0	2	25	0	0	0	0	1	0	1	
$H(\text{C}-\text{Au}-\text{C})$	0	0	0	0	2	0	6	49	0	0	0	0	0	0	0	
$H(\text{H}-\text{C}-\text{H})$	0	0	94	57	7	5	0	0	0	0	94	58	7	6	0	
$H(\text{H}-\text{C}-\text{Au})$	0	0	2	6	11	1	0	0	0	0	1	6	11	1	0	
$F(\text{Au}\cdots\text{H})$	4	4	3	33	78	27	0	2	4	4	4	33	79	28	0	
$F(\text{H}\cdots\text{H})$	0	1	2	1	0	0	0	0	0	1	2	1	0	0	0	
$F(\text{C}\cdots\text{C})$	0	0	0	0	0	2	1	7	0	0	0	0	0	0	0	
$F(\text{Cl}\cdots\text{Cl})$	0	0	0	0	0	0	11	0	0	0	0	0	0	0	0	
$F(\text{Cl}\cdots\text{C})$	0	0	0	0	0	1	1	10	0	0	0	0	0	1	2	

frequencies are collected in Table IX. The potential energy distribution for $(\text{CH}_3)_2\text{AuCl}_2^-$ which is typical for these ions is tabulated in Table X. Table XI provides a comparison of the stretching force constants of the different $(\text{CH}_3)_2\text{AuL}_2^-$ ions and Table XII contrasts the Au-X stretching force constants of the AuX_4^- and $(\text{CH}_3)_2\text{AuX}_2^-$ ions.

A Critique of the Calculations.—The analysis of the vibrations of large ions like these is to some extent a case of "inorganic chemists rushing in where spectroscopists fear to tread." Since the labor involved in setting up the calculations is not trivial and appreciable amounts of computer time are consumed, it seems worthwhile to examine the pros and cons of such efforts.

TABLE XI

VALENCE STRETCHING FORCE CONSTANTS^a FOR $(\text{CH}_3)_2\text{AuL}_2^-$ IONS AND THE $J(^{13}\text{C}-\text{H})$ COUPLING CONSTANTS (STANDARD ERRORS IN PARENTHESES)

	$(\text{CH}_3)_2\text{-AuCl}_2^-$	$(\text{CH}_3)_2\text{-AuBr}_2^-$	$(\text{CH}_3)_2\text{-Au(OH)}_2^-$	$(\text{CH}_3)_2\text{-Au(OH)}_2^+$
$F_{\text{dia}}(\text{Au}-\text{C})$, mdyn/Å	2.81 (0.06)	2.72 (0.09)	2.96 (0.07)	3.01 (0.09)
$F_{\text{dia}}(\text{Au}-\text{L})$, mdyn/Å	1.38 (0.08)	1.22 (0.15)	1.82 (0.07)	1.62 (0.08)
$F_{\text{dia}}(\text{C}-\text{H})$, mdyn/Å	4.85 (0.03)	4.87 (0.04)	4.88 (0.05)	4.90 (0.06)
$J(^{13}\text{C}-\text{H})$, Hz	139	139	136	141

^a Obtained by transformation from the Urey-Bradley field.

TABLE XII

COMPARISON OF THE Au-X VALENCE STRETCHING FORCE CONSTANTS^a FOR $(\text{CH}_3)_2\text{AuX}_2^-$ AND AuX_4^- ANIONS (STANDARD ERRORS IN PARENTHESES)

Anion	$F_{\text{dia}}(\text{Au}-\text{X})$, mdyn/Å	Anion	$F_{\text{dia}}(\text{Au}-\text{X})$, mdyn/Å
AuCl_4^-	2.15 (0.29)	AuBr_4^-	1.82 (0.13)
$(\text{CH}_3)_2\text{AuCl}_2^-$	1.38 (0.08)	$(\text{CH}_3)_2\text{AuBr}_2^-$	1.22 (0.15)

^a Obtained by transformation from the Urey-Bradley field.

By a coordination chemist's standards, dichlorodimethylaurate(III) is quite a simple anion, and it is closely related to metal-amine complexes for which somewhat less extensive calculations have been made by several groups. The infrared spectrum was surveyed from 33 to 4000 cm^{-1} and the Raman spectrum from ca. 175 to 3500 cm^{-1} . Nevertheless, two of the in-plane fundamentals which occurred below 200 cm^{-1} were not observed. The case was even less favorable with the other ions.

The UBFF works well, since coupling is minimal because of the massive gold atom and the orthogonality of the two gold-carbon and the two gold-ligand bonds. This is seen from the data in Table X. These calculations show that skeletal stretching frequencies should be indicators of trends in the strengths of the skeletal bonds in analogous molecules and ions. When comparing the strengths of bonds from gold to Cl^- , Br^- , OH^- , etc., some sort of a force constant clearly is necessary.

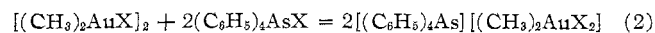
For these square-planar complexes, there is a redundancy involving the skeletal bond angles, but it is exact to the first order. Consequently, force constants of different molecules describing in-plane vibrations are, at least theoretically, comparable. The assumption of $\kappa = 0$ is equivalent to assuming that the redundancies in the angles about the carbon atoms are exact in the first order which is not strictly true. Nevertheless, the error caused is apparently not serious, since values of $K(\text{C}-\text{H})$ calculated assuming $\kappa = 0$ for a series of organometallic compounds of the representative elements correlate very well with carbon-13-proton coupling constants.³⁸

In the calculations on the AuX_4^- and $(\text{CH}_3)_2\text{AuX}_2^-$ ions, the force fields have been kept similar in the hope that the errors will tend to cancel when force constants are compared. The reader should not be deceived into comparing the numerical values reported here with ones for similar molecules computed using different force fields.

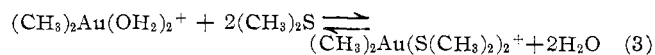
A minor problem arises in the operations on the large matrices involved. The tolerance set in many standard matrix diagonalization subroutines to test the off-diagonal elements is sufficiently large so that significant computational errors may arise, especially when some of the eigenvalues are degenerate. Since in the standard programs³⁴ G is diagonalized first, the W matrix is computed and used to transform F , and this matrix is then diagonalized, errors tend to accumulate. Consequently, it is wise to experiment with the tolerance values to ensure that sufficient accuracy is attained to give calculated frequencies within 1 cm^{-1} of the correct value.

Discussion

The di- μ -halogeno bridges of the dimethylgold(III) halides are readily cleaved by excess halide ion to give *cis* complex anions according to



In the presence of Ag^+ , these complex halide anions aquate very rapidly in aqueous solution producing the stable aquo cation, *cis*- $(\text{CH}_3)_2\text{Au}(\text{OH}_2)_2^+$. Equilibration with neat dimethyl sulfide leads to the substitution of the water molecules by two $\text{S}(\text{CH}_3)_2$ (eq 3), but in the absence of excess ligand, the complex slowly decomposes to yield the aquo cation once more. The



diammine complex $[(\text{CH}_3)_2\text{Au}(\text{NH}_3)_2]\text{Cl}$ can also be produced with excess ligand, but it loses 1 mol of ammonia readily. Chemically the bonds from gold to the ligands other than the methyl groups are relatively weak and substitution occurs rapidly at these positions in contrast to the AuX_4^- ions which are much less labile.³⁹ This effect of the alkyl groups in labilizing the other ligands in the first coordination sphere is much more obvious in the trimethylplatinum(IV) cation.^{13,40}

An examination of the gold-carbon stretching and methyl deformation frequencies listed in Table III shows that approximately the same *trans* influence series operates with these Au(III) complexes as has been established from studies on the isoelectronic Pt(II), *i.e.*, the ligands decrease in their *trans* influence in the order $(\text{CH}_3)_2\text{S} > \text{Br}^- > \text{Cl}^- > \text{en} > \text{OH}^- > \text{H}_2\text{O}$. The variation in the symmetric methyl deformation frequencies parallels that of the skeletal Au-C₂ stretching frequencies, and this was also observed to be the case with dimethylplatinum(II) compounds.⁴¹ Since the mass of the gold atom is so large, the variation in $\delta_s(\text{CH}_3)$ probably reflects changes in the H-C-Au bending force constant, since some slight coupling usually occurs between the methyl deformation and rocking modes.⁴² The increase in frequencies from the dimethyl sulfide complex to the aquo cation is consistent with increasing effective electronegativity of the gold atom in this sequence. A much more striking effect is the decrease in the Au-X stretching frequency caused by replacement of two halide ions of AuX_4^- with two "methide" ions. This results in a drop of almost 20% in the highest Au-Cl stretching frequencies.

In order to examine these effects more precisely, the normal-coordinate calculations were carried out. Although the UBFF is not a very good model for the

AuX_4^- anions, it is quite satisfactory for the $(\text{CH}_3)_2\text{AuX}_2^-$ ions. Substitution of two methide ions for two halides reduces the coupling in the structure. In the following discussion, comparisons will be made only among the skeletal stretching force constants and more particularly among the appropriate diagonal elements of the *F* matrix expressed in the internal coordinates. The calculated values of these constants were little influenced by the various modifications of the force fields which were tried.

The data in Tables VIII and XI also show the decreasing *trans* influence of the ligands in the sequence $\text{Br}^- \simeq \text{Cl}^- > \text{OH}^- \simeq \text{H}_2\text{O}$. The ligands giving the strongest Au-C bonds, OH^- and H_2O , also form the strongest bonds to the gold(III). From this it can be concluded that the most energetically favorable situation is where the two additional ligands are bound to $(\text{CH}_3)_2\text{Au}^+$ by primarily electrostatic interactions. Very little change is observed in the C-H stretching force constants or in the carbon-13-proton coupling constants as the inorganic ligands bound to gold are varied.

The effect which the methyl groups exert on the inorganic ligands in the first coordination sphere is particularly apparent from the data on the Au-X stretching force constants of Table XII. Replacement of two chlorides by two CH_3^- causes a decrease of 36% in the Au-Cl stretching force constant, while the corresponding decrease in the Au-Br constant is 33%.

It can be concluded that the dialkylgold(III) moieties are stabilized by highly electronegative ligands which undergo primarily coulombic interactions with them. This is in marked contrast to the isoelectronic dialkylplatinum(II) compounds which are stabilized by polarizable ligands like phosphines or arsines.

The $\text{Au}(\text{CN})_2\text{X}_2^-$ ions apparently are exclusively *trans*,²² while the $(\text{CH}_3)_2\text{AuX}_2^-$ ions have exclusively the *cis* structure. The Au-Cl stretching force constant appears to be slightly greater in *trans*- $\text{Au}(\text{CN})_2\text{Cl}_2^-$ than in AuCl_4^- , while it is markedly smaller in *cis*- $(\text{CH}_3)_2\text{AuCl}_2^-$. Although cyanide ion generally is put higher than methide in the *trans*-effect series based on the behavior of platinum(II) complexes, the stereochemical effects of substituting CH_3^- and CN^- for Cl^- in AuCl_4^- would suggest that the opposite is true. For gold(III), π -bonding effects presumably would be less important than with platinum(II).

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