On the other hand, thiourea and $SeCN^-$, and NO_2^- to a lesser extent, show significant values of Δ. The quantity which, by definition, is zero for the standard complex *trans*-$[Pt(py)_2Cl_2]$ becomes negative when cationic complexes are used as substrates and also in the reactions of the neutral complexes containing phosphine ligands, in which π interactions can delocalize charge from the reaction center. In the reactions on $[PtCl_4]^{2-}$ the deviations are positive so that the over-all behavior strongly suggests that back-donation of charge from the metal to those entering groups can decrease the activation free energy.

It should be pointed out that, whereas the presence of a significant value of Δ and its dependence upon the electronic density at the reaction center is good evidence for biphilic behavior, one cannot compare the values of Δ for different reagents arguing, for example, that, because of the greater value of Δ, thiourea has a greater biphilic ability than NO_2^-. In fact, the actual deviations must also be related to the degree of formation of the new bond in the transition state which may be different for the various entering reagents even though all the reactions are bimolecular second-order processes.

From the above argument one can conclude that, as far as reactions of Pt(II) substrates are concerned, the potential entering ligands can be divided into four groups according to their behavior. In the first, the nucleophiles exibit a sequence of relative reactivity that is practically independent of the nature of the Pt(II) substrate. The basicity plays a minor role, negligible in most cases, so that in this group the values of n_{Pt} can be mainly regarded as an index of softness which is probably related to high micropolarizability, which "...results from the existence of low-lying excited states, which, when mixed with the ground state, produce polarity."[1]

In the second group one can consider reagents in which the empty, low-lying orbitals not only contribute to the softness but also have the right symmetry and energy to contribute to the stabilization of the transition state by a direct overlap with the filled d orbitals of the metal. The position of such reagents (NO_2^-, thiourea, $SeCN^-$) in the sequence of relative reactivity appears to be influenced by the charge and nature of the Pt(II) substrate. The requirement that the empty orbitals used for back-donation must have the right energy to give a good overlap may explain why $SeCN^-$ has biphilic properties whereas N_3^- and SCN^-, with similar outer electronic configurations, do not. Although adequate kinetic data are not yet available, it seems reasonable to predict that reagents such as PR_3, olefins, allyl alcohol, and carbon monoxide would fit into this group.[20]

The third group contains those nucleophiles that are hard and, even when strongly basic, do not react with Pt(II) complexes, *e.g.*, F^-, OH^-, CH_3O^-.

Finally, there are some species, such as HNO_2 and H_3BO_3, for which back-donation of charge *via* π bonding is the most important factor. These can act as catalysts[13] in substitution reactions in a way that can best be regarded as an electrophilic attack on the metal, which, in such cases, functions as a Lewis base.

Acknowledgments. We thank Dr. M. L. Tobe for helpful stimulating discussions.

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[20] NOTE ADDED IN PROOF. Recent results on the reactions of allyl derivatives seem to agree with the idea pointed out here (L. Venanzi, private communication).

Structure of Dimethylgold(III) Compounds. Spectroscopic Studies on the Aquo Ion and Several Coordination Compounds[1]

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Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received July 5, 1966*

Abstract: Dimethylgold(III) hydroxide has been synthesized and used to prepare aqueous solutions of $(CH_3)_2AuNO_3$, $(CH_3)_2AuClO_4$, and $Na[(CH_3)_2Au(OH)_2]$. Raman and pmr spectra indicate that the aquo ion and the hydroxo complex exist in solution exclusively as the *cis* isomer. For comparison, 2,4-pentanedionatodimethylgold(III), dimethyl(ethylenediamine)gold(III) iodide, and di-μ-iodo-tetramethyldigold have been synthesized and their Raman, infrared, and pmr spectra determined. The vibrational frequencies of dimethylgold(III) are compared with those of the isoelectronic dimethylplatinum(II) and also with the dimethylthallium(III) moieties.

Only a relatively small number of organogold(III) compounds have been synthesized, and most of our knowledge of these stems from the research of Gibson and co-workers. Among the compounds prepared are the dialkylgold(III) halides $(C_2H_5)_2AuBr$,[3,4] $(CH_3)_2AuBr$,[5] and $(CH_3)_2AuI$,[5] together with the ethylenediamine chelates of dimethylgold(III),[5]

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[2] (a) Research Fellow in Chemistry; (b) NASA Predoctoral Fellow.

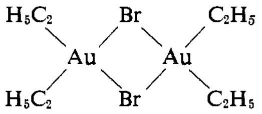
[3] C. S. Gibson and W. M. Colles, *J. Chem. Soc.*, 2407 (1931).

[4] A. Burawoy and C. S. Gibson, *ibid.*, 860 (1934).

[5] F. H. Brain and C. S. Gibson, *ibid.*, 762 (1939).

diethylgold(III),[6] di-*n*-propylgold(III),[3,7] di-*n*-butylgold(III),[3] and some gold heterocycle moieties.[8,9] Dimethylgold acetylacetonate was also prepared.[5] Several of the structures suggested initially for these compounds were incorrect and were revised in a later communication.[10]

A single crystal X-ray study of $(C_2H_5)_2AuBr$ which is dimeric in organic solvents confirmed the expected square-planar coordination about gold(III); that is, the compound is di-μ-bromo-tetraethyldigold (I).[11]



I

The compound $[(C_2H_5)_2Au]_2SO_4$ was also prepared,[12] and cryoscopic measurements on an aqueous solution indicated the presence of three ions per $[(C_2H_5)_2Au]_2SO_4$ formula unit. It therefore was presumed that square-planar diaquodiethylgold(III) cations together with free sulfate ions were present.

Studies of the structure in aqueous solution of several ions of the type $(CH_3)_2M^{2+}$ have been made recently using Raman spectroscopy for the cases where M = Sn(IV),[13] Tl(III),[14] and Pb(IV).[15,16] As described in a recent review,[17] these ions interact rather weakly with water molecules in the first coordination sphere and are present in acidic solutions as the unhydrolyzed aquo ions. They appear to adopt the *trans* configuration exclusively.

There are very few transition metal organometallics with σ metal–carbon bonds which give stable aquo cations. The ion $(CH_3)_2Au^+$, analogous to the aforementioned $(C_2H_5)_2Au^+$, appears to be the only one of the $(CH_3)_2M^{2+}$ type. The gold d^8 electronic configuration differs from $(CH_3)_2Tl^+$ and $(CH_3)_2Pb^{2+}$ only by two 5d electrons. Comparison of these ions should allow an evaluation of the effect of the incomplete d subshell on the structure and properties of the organometallic moiety. In addition, the dimethylgold(III) ion should permit a detailed study of the gold–oxygen bond and, in particular, of water molecules coordinated directly in trivalent gold.

The $(CH_3)_2Au^{III}$ and $(CH_3)_2Pt^{II}$ moieties are isoelectronic, and comparable geometrical isomers should be isostructural. In practice, it has been possible to synthesize only the *cis*-dimethylplatinum(II) compounds and then only when the other two coordination sites in the square plane are occupied by tertiary phosphines or similar ligands.[18] In contrast, the dimethylgold(III) moiety is found with halide, oxygen, or nitrogen donors in the other coordination sites, although the lack of reactivity of the di-μ-thiocyanato-tetramethyldigold indicates that the dimethylgold(III) moiety can also be stabilized by heavier group VI donor atoms.[19] Several studies have been made of the vibrations of the *cis*-dimethylplatinum(II) moiety, and it was of interest to compare these vibrational frequencies and assignments with those of dimethylgold(III). With these objectives in mind, the Raman and infrared spectra of several dimethylgold(III) compounds have been obtained.

Experimental Section

Syntheses. All of the compounds were synthesized several times. Analyses for C and H in these rather unstable compounds were performed by the Microanalytical Laboratory, Department of Chemistry, University of Minnesota.

Dimethylgold Iodide.[5] This was prepared from trichloro(pyridine)gold(III) by the method of Brain and Gibson,[5] yield 35%. The observed melting point was 95–96° dec; lit.[5] 78.5°. *Anal.* Calcd for C_2H_6AuI: C, 6.78; H, 1.69; I, 35.9. Found: C, 7.05; H, 1.90; I, 36.3. The compound detonates readily upon grinding.

Dimethyl(ethylenediamine)gold(III) Iodide.[5] This was prepared from dimethylgold(III) iodide by the method of Brain and Gibson,[5] mp 169°, lit.[5] 168°.

Dimethylgold(III) Hydroxide. Dimethylgold(III) iodide (5.3 g, 0.015 mole) was dissolved in 100 ml of ligroin (bp 60–80°), and a solution of silver nitrate (0.02 mole) in 100 ml of 0.001 *M* nitric acid was added. The mixture was stirred virgorously, and the ligroin was removed slowly at room temperature. The aqueous phase was filtered, treated with excess sodium hydroxide, and stirred for 30 min. At this stage the dimethylgold(III) is in solution, presumably as $[(CH_3)_2Au(OH)_2]^-$, and excess silver ion is precipitated. The Ag_2O was filtered off; $(CH_3)_2AuOH$ was precipitated from the filtrate by adding 2 *M* nitric acid, collected, washed with water, and dried under vacuum over P_4O_{10} at 0°, yield 90%. Proton magnetic resonance spectra in anhydrous organic solvents indicate that the compound contains traces of water which cannot be removed easily. It decomposes slowly above 120° and detonates at *ca.* 150° upon rapid heating. *Anal.* Calcd for C_2H_7AuO: C, 9.84; H, 2.89. Found: C, 10.4; H, 3.12. The hydroxide which is only very slightly soluble in water dissolves readily in either strong acids or strong bases.

2,4-Pentanedionatodimethylgold.[5] Dimethylgold hydroxide (2.5 g, 0.01 mole) was dissolved in 2 *M* sodium hydroxide and treated with acetylacetone (1.2 g, 0.012 mole). The solution was slowly neutralized with 6 *M* nitric acid, and the precipitated $(CH_3)_2Au$-(acac) was washed with water, dried under vacuum at 0°, and recrystallized from ligroin, yield 86%. The observed melting point was 80–81°, lit.[5] 84°. *Anal.* Calcd for $C_7H_{13}O_2Au$: C, 25.8; H, 4.02. Found: C, 26.0; H, 4.15.

Dimethylgold(III) Nitrate and Perchlorate Solutions. Dimethylgold(III) hydroxide was dissolved in standard nitric or perchloric acid to give solutions containing a slight excess of the free acid. Because of the combination of the excellent oxidizing properties of Au(III) and the perchlorate or nitrate ions with the oxidizable alkyl groups, the pure compounds were not isolated from the solutions.

Sodium Dihydroxodimethylaurate(II) Solution. Dimethylgold hydroxide was dissolved in standard sodium hydroxide to give a solution containing excess free base.

Raman Spectra. All spectra were obtained with a Cary 81 spectrophotometer. The solution spectra were run at 0° by pumping water through a jacket surrounding the 7-mm Raman cell. The general procedure was similar to that employed in earlier work.[13] Gelman Metricel-VM polyvinyl ultrafilters were used to clarify the solutions. Spectra of microcrystalline powders were obtained using a conical cell. This was maintained at *ca.* 5° by surrounding it with a jacket and passing cold nitrogen over the cell.

Although survey spectra could be obtained for the solutions in a sufficiently short time so that no appreciable decomposition took place, this was not the case during the attempts to obtain accurate integrated intensities and during the polarization measurements. These required irradiation of the samples for periods of hours, and decreases in intensity together with the formation of traces of

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Table I. Raman Shifts of 2.25 *M* Dimethylgold(III) Nitrate, 2.61 *M* Dimethylgold(III) Perchlorate, and 0.74 *M* Sodium Dihydroxodimethylaurate(III) in Aqueous Solutions

2.25 *M* $(CH_3)_2AuNO_3$[a]			2.61 *M* $(CH_3)_2AuClO_4$[b]			0.74 *M* $Na[(CH_3)_2Au(OH)_2]$[c]			
ν, cm^{-1}	I[d]	ρ[e]	ν, cm^{-1}	I[f]	ρ[g]	ν, cm^{-1}	I[d]	ρ[e]	Assignment
275	114	0.51	274	113	0.54	267	. . .[h]	. . .[h]	$\delta(Au-C_2)$
406	94	0.07	418	179	0.11	441	~200	0.3	$\nu(Au-O_2)$
			466	145	0.83				$\nu_2(ClO_4^-)$
591	1000	0.42	591	1000	0.25	586	1000	0.53	$\nu(Au-C_2)$
			633	92	0.90				$\nu_4(ClO_4^-)$
719	14	. . .							$\nu_4(NO_3^-)$
876 bd	35	. . .							$\rho_r(CH_3)(Au-CH_3)$
			933	311	0.0				$\nu_1(ClO_4^-)$
1049	310	0.27							$\nu_1(NO_3^-)$
			~1120	. . .[h]	. . .[h]				$\nu_3(ClO_4^-)$
1222	93	. . .	1222	115	0.47	1220	143	dp	$\delta_s(CH_3)(Au-CH_3)$
1258	65	. . .	1260	76	0.14	1249	89	p	$\delta_s(CH_3)(Au-CH_3)$
1422 bd	135	. . .							$\nu_3(NO_3^-)$
2926	302	. . .	2927	414	0.05	2914	177	p	$\nu_s(C-H)(Au-CH_3)$
3016	136	. . .	3012	154	0.91	3004	42	dp	$\nu_{as}(C-H)(Au-CH_3)$

[a] The solution contains *ca.* 0.25 *M* excess HNO_3. [b] The solution contains *ca.* 0.05 *M* excess $HClO_4$. [c] The solution contains *ca.* 1.26 *M* excess NaOH. [d] Uncorrected integrated intensities relative to the intensity of the 591-cm^{-1} line = 1000. [e] Observed uncorrected values. bd = unusually broad lines, p = polarized, dp = depolarized. [f] Integrated intensities relative to the intensity of the 591-cm^{-1} line = 1000; corrected for decomposition according to $I = I_{exptl}\exp(0.00861\ min^{-1}\ t)$. [g] Corrected for decomposition by $I_\perp = I_{\perp,exptl}\exp(0.0019\ min^{-1}\ t)$ and $I_\parallel = I_{\parallel,exptl}\exp(0.0022\ min^{-1}\ t)$; corrected values obtained with $\alpha = 0.274$, $\beta = 0$. [h] Intensity too low to measure.

colloidal gold as a function of time were observed. Integrated intensities were obtained from the spectra with a Gelman planimeter. The measured intensities were corrected empirically to time $t = 0$ by assuming that to a first approximation the change in intensity with time obeyed the first-order rate equation, $I_0 = I\exp(kt)$ where I_0 and I were the intensities at $t = 0$ and at the time of the measurement, respectively. The parameter k was evaluated from measurements of the intensity of the most intense line in the spectrum at the beginning and end of a particular scan.

Since knowledge of the state of polarization of the lines was important for a correct determination of the aquo-ion structure, efforts were made to obtain the values of the depolarization ratios as precisely as possible. First it was necessary to correct the intensities obtained with the crossed and axial polarizers for decomposition as outlined above. Secondly, it was necessary to correct for instrumental errors such as the nonparallel nature of the exciting light. Attempts to use baffles together with the polaroids required very high sensitivity settings and gave a poor signal-to-noise ratio. The depolarization ratios were obtained for the solutions without baffles and were corrected empirically with eq 1.

$$\rho = \frac{I_\parallel - \alpha I_\perp}{I_\perp - \beta I_\parallel} \qquad (1)$$

Here $I_\parallel$ refers to the integrated intensity with the axial polarizer in place, $I_\perp$ is the integrated intensity with the crossed polarizer, and α and β are constants. In general, the values of α and β are obtained by solving the pair of simultaneous equations in the depolarization ratios of the 938- and 1120-cm^{-1} lines of the spectrum of perchlorate taken as an internal standard. This anion has little tendency to coordinate, and the dimethylgold(III) solutions show the lines of the free perchlorate ion. The perchlorate ion belongs to point group T_d, and the symmetry species of the normal modes giving the 938- and 1120-cm^{-1} Raman shifts are A_1 (ν_1) and F_2 (ν_3), respectively. Thus the correct depolarization ratios, ρ, for these two lines are 0 and 0.857. Using this technique the depolarization ratios calculated for the 465 (E, ν_2) and 632 (F_2, ν_4) lines of a 7 *M* $NaClO_4$ solution were 0.84 and 0.88. The uncorrected ρ values were ν_1 0.219, ν_2 0.91, ν_3 0.92, and ν_4 0.94.

Infrared Spectra. A Perkin-Elmer Model 521 grating spectrometer was used, and the spectra were obtained using the split mull technique and KBr or CsI windows. Calibration of the instrument was effected with polystyrene film. Spectra were recorded for several different samples of each compound in order to eliminate spurious bands.

Proton Magnetic Resonance Spectra. A Varian A-60 spectrometer was used, and coupling constants and chemical shifts were determined by the side-band technique. Coupling constants are believed to be accurate to ±0.5 cps and the chemical shifts to ±0.01 ppm.

Data and Results

Raman Spectra of Dimethylgold(III) Nitrate and Perchlorate and Sodium Dihydroxodimethylaurate(III) in Aqueous Solutions. Values for the Raman shifts observed for the solutions of $(CH_3)_2AuNO_3$, $(CH_3)_2AuClO_4$, and $Na[(CH_3)_2Au(OH)_2]$ are listed in Table I together with the integrated intensities and depolarization ratios. The spectra of $(CH_3)_2AuNO_3$ and $(CH_3)_2AuClO_4$ consist of the spectrum of the aquodimethylgold(III) species superimposed on that of free, that is uncoordinated, nitrate or perchlorate ion. The spectrum of $(CH_3)_2AuNO_3$ is illustrated in Figure 1.

Raman and Infrared Spectra of 2,4-Pentanedionatodimethylgold and Dimethyl(ethylenediamine)gold(III) Iodide. The Raman and infrared spectra of $(CH_3)_2Au(acac)$ are listed in Table II. Infrared frequencies are also listed for $[(CH_3)_2AuI]_2$. Because this compound photolyzes rapidly, a Raman spectrum could not be obtained. The assignments of the acetylacetonate vibrations, which are typical for chelates, were made by comparison with the Raman and infrared spectra of bis(2,4-pentanedionato)dimethyltin[20] and are based on the normal coordinate analysis of Nakamoto.[21]

The Raman and infrared frequencies for $[(CH_3)_2Au(en)]I$ are tabulated in Table III. The assignments for the ethylenediamine ligand are made by comparison with the spectra of ethylenediamine complexes of platinum(II) reported by Powell and Sheppard[22] and the Raman and infrared spectra of several ethylenediamine complexes recently published by Krishnan and Plane.[23]

Proton Magnetic Resonance Spectra. The results of the measurements of the pmr of several dimethylgold(III) compounds are listed in Table IV.

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Table II. Raman and Infrared Spectra of 2,4-Pentanedionatodimethylgold and the Infrared Spectra of Di-μ-iodo-tetramethyldigold

Infrared, $[(CH_3)_2AuI]_2$, mull	Infrared, $(CH_3)_2$-Au(acac), mull	Raman, $(CH_3)_2$-Au(acac), crystal powder[b]	Assignment
ν, cm^{-1} [a]			
		204 w	acac
		268 m	$\delta(Au-C_2)$
	444 vs	445 vs	$\nu(Au-O_2)$
		559 w	πacac
	584 w	585 vvs	$\nu(Au-C_2)$
	610 w		πacac
	648 s		$\delta(C-CH_3) + (M-O)\ (B_2)$
	684 s	692 w, bd	$\nu(\text{ring deformn} + (M-O))\ (A_1)$
	776 vs		$\pi(C-H)$acac
800 w, bd	829 m		$\rho_r(CH_3)(Au-CH_3)$
	929 s	931 w, bd	$\nu(C-CH_3) + (C-O)\ (A_1, B_2)$
	1023 vs		$\rho_r(CH_3)$acac
1188 m, sh	1197 s	1201 m	$\delta_s(CH_3)(Au-CH_3)$
	1207 vw		$\delta(C-H)$acac (B_2)
1220 m, sh	1236 s	1240 w	$\delta_s(CH_3)(Au-CH_3)$
	1264 vs	1270 vs	$\nu(C-C) + \nu(C-CH_3)\ (A_1)$
	1335 m	1359 m, bd	$\delta_s(CH_3)$acac
	1392 vs		$\delta_d(CH_3)$acac
1400 w, bd	(1400)[c]		$\delta_{as}(CH_3)(Au-CH_3)$
	1421 m		$\nu(C-O) + \delta(C-H)\ (B_2)$
	1520 vvs		$\nu(C-O)\ (A_1)$
	1590 vvs		$\nu(C-C)\ (B_2)$
2813 w	2813 vw		$\nu_s(C-H)(Au-CH_3)$
2904 m, sh	2915 m, sh	2915 s	$\nu_s(C-H)$
3000 w, bd	2985 m	2990 m	$\nu_{as}(C-H)(Au-CH_3)$
		3088 w	$\nu(C_3-H)$acac

[a] v = very, w = weak, m = medium, s = strong, sh = sharp, bd = broad. [b] Spectrum obtained at approximately 5°. [c] Hidden by 1392-cm^{-1} band.

The τ values of the γ_{C-H} and methyl protons of the ligand in $(CH_3)_2Au(acac)$ were 4.69 and 8.02 which may be compared with the corresponding values of $(CH_3)_2Tl(acac)$, 4.88 and 8.12 ppm, respectively,[24] and of $(CH_3)_2Sn(acac)_2$, 4.73 and 8.06, respectively.[20]

Discussion

All of the dialkylgold(III) compounds which have been prepared are either mononuclear chelates or polynuclear complexes with the methyls of necessity *cis* to one another in square-planar coordination. It is therefore first necessary to consider whether hydrolysis of di-μ-iodo-tetramethyldigold, in which the methyl groups are *cis* to each other, to the hydroxide followed by dissolution in acids or bases occurs with isomerization, with retention of the *cis* configuration, or whether the solutions contain appreciable concentrations of both isomers.

The pmr spectra of the aqueous solutions of $(CH_3)_2AuNO_3$, $(CH_3)_2AuClO_4$, and $Na[(CH_3)_2Au(OH)_2]$ all exhibit a single, sharp methyl signal. The Raman spectra of the solutions show only a single, sharp, symmetrical, polarized line due to symmetrical $Au-C_2$ bond stretching. These data indicate the existence of a single isomer, although the symmetrical stretching frequencies of *cis* and *trans* isomers might be accidentally degenerate and rapid isomerization would produce a single methyl pmr signal.

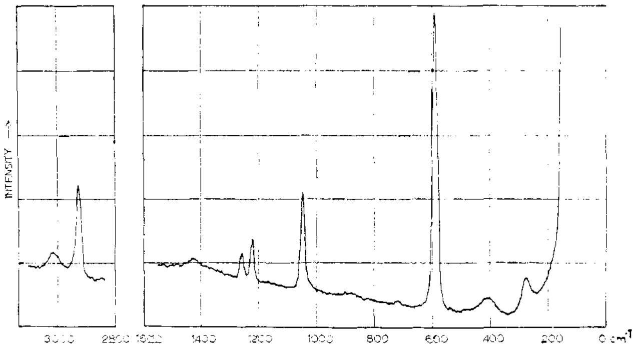

Figure 1. Raman spectrum of aqueous 2.25 *M* dimethylgold(III) nitrate.

For the purpose of assigning the Raman spectra, a five-atom model with the methyl groups taken as single masses was used for the skeletal modes. With a very heavy central atom like gold, the methyl groups tend to vibrate as single masses in the skeletal modes. The representations of the normal skeletal vibrations for the *cis* C_{2v} and *trans* D_{2h} configurations are given by eq 2 and 3. On the basis of these, a *trans* configuration

Table III. Raman and Infrared Spectra of Dimethyl(ethylenediamine)gold(III) Iodide

Raman, crystal powder	Infrared, mull	Assignment
ν, cm^{-1} [a]		
	240 m	$\delta(Au-C_2)$
	280 w	Chelate ring bend
	405 m	
480 s	490 m	$\nu(Au-N_2)$
	535 s	
580 vvs	570 w	$\nu(Au-C_2)$
	718 m	
	821 w	NH_2 rock
870 vw	867 w	en
	996 m	NH_2 twist
	1050 vs	Ring skeletal
	1097 w, sh	Ring skeletal
	1112 s	NH_2 twist
	1159 m	NH_2 twist
1220 m	1206 m	$\delta_s(CH_3)(Au-CH_3)$
1245 m	1238 m	$\delta_s(CH_3)(Au-CH_3)$
	1279 m	CH_2 twist
	1315 vw	NH_2 wag
	1364 w	CH_2 wag
	1395	CH_2 wag
	1412	
	1450	CH_2 scissors
1465 w	1460 w	CH_2 scissors
	1582 s	NH_2 scissors
	2802 vvs	C–H stretch
	2858 vvs	C–H stretch
2905 s	2908 m	C–H stretch
2920 vs		C–H stretch
2965 vs, bd	2960 w, bd	C–H stretch
	3113 vvs	NH_2 stretch
	3194 vvs	NH_2 stretch

[a] Abbreviations are the same as in Table II.

$$\Gamma_{cis} = 4A_1 + A_2 + B_1 + 3B_2 \text{ (molecule in } \sigma_{yz}) \quad (2)$$

$$\Gamma_{trans} = 2A_g + B_{1g} + 2B_{1u} + 2B_{2u} + 2B_{3u} \text{ (molecule in } \sigma_{xy}) \quad (3)$$

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Table IV. Chemical Shifts and Coupling Constants of the Methyl Protons of Some Dimethylgold(III) Compounds

Compound	Solvent	Concn, m	$\tau^{a,c}$ (CH_3–Au)	J^{13} (C–H)
$[(CH_3)_2AuI]_2{}^b$	$CHCl_3$	Satd	8.46	142.5
$(CH_3)_2AuNO_3$	0.25 M HNO_3	2.25	8.78	. . .
$(CH_3)_2AuClO_4$	0.05 M $HClO_4$	2.61	8.78	141.2
$(CH_3)_2Au(acac)$	$CHCl_3$	0.49	8.86	140.9
$Na[(CH_3)_2Au(OH)_2]$	1.26 M NaOH	0.75 (satd)	9.32	135.8

[a] Temperature 40°. [b] The sample decomposed rapidly at 40° with the growth of a signal at 9.17 ppm; spectrum obtained at $-17°$. [c] τ(tetramethylsilane) = 10 for nonaqueous, τ(trimethylsilylpropane sulfonate) = 10 for aqueous solutions.

would be expected to give three Raman lines, two of which should be polarized; while the *cis* configuration would give nine Raman lines with four polarized. Unfortunately, with a heavy central atom in a complex, extensive accidental degeneracy is the rule, and the bending modes are very low in frequency. This coupled with the low Raman intensity associated with certain vibrations almost always leads to fewer than the predicted number of lines being observed.

In the spectra of the aquo ion, the Raman shifts above 1000 cm^{-1} clearly result from internal vibrations of the methyl groups. The very weak line observed at 876 cm^{-1} in the nitrate solution is about the right frequency for a methyl rocking vibration.

The presence of three polarized lines at lower frequencies is only in accord with the *cis* structure.

The four expected totally symmetrical vibrations include, qualitatively, symmetrical Au–C_2 stretching, symmetrical Au–O_2 stretching, and two in-plane bending modes which with loosely associated water molecules would be primarily Au–C_2 bending. These latter two might well be accidentally degenerate which would account for the presence of only three polarized lines.

The polarized 591-cm^{-1} line must arise primarily from symmetrical gold–carbon bond stretching, the very broad, polarized line at 406–418 cm^{-1} is typical of those resulting from metal–oxygen bond stretching involving coordinated water molecules,[25] and the polarized 274–275 cm^{-1} line corresponds approximately to that expected for a skeletal deformation. The observation of only a single sharp line for Au–C_2 stretching would tend to indicate a *trans* structure were it not for the fact that the totally and nontotally symmetrical Pt–C_3 stretching vibrations of $(CH_3)_3Pt^+$ appear to be accidentally degenerate.[26] The stretching of bonds to coordinated water molecules normally gives a very broad line, and Raman shifts due to symmetrical and antisymmetrical modes have not been resolved.

The remaining lines expected, all depolarized, would be described qualitatively as antisymmetrical Au–C_2 and Au–O_2 stretching (B_2), in-plane C–Au–O bending (B_2), and two out-of-plane bending modes (A_2, B_1). The in-plane C–Au–O bending mode is probably degenerate with the totally symmetrical mode at 274–275 cm^{-1}. Finally the remaining bending modes may have very low frequencies and occur beyond the range of these measurements, that is, shifts less than 175 cm^{-1}.

The spectra of the dimethylgold(III) moiety were obtained for other compounds where it has the *cis* configuration: di-μ-iodo-tetramethyldigold, dimethylgold(III) acetylacetonate, and dimethyl(ethylenediamine)gold(III) iodide. The vibrations of both the acetylacetonate and ethylenediamine ligands are typical for chelates. Only a single, sharp line assignable to Au–C_2 stretching was observed in the Raman spectra of the acetylacetonate and ethylenediamine complexes at 585 and 580 cm^{-1}, respectively, compared to 591 cm^{-1} for the aquo ion. The line assigned to a vibration involving predominantly AuC_2 bending is observed at 274, 268, and 240 cm^{-1} in $(CH_3)_2Au^+$, $(CH_3)_2Au(acac)$, and $[(CH_3)_2Au(en)]I$, respectively. The observed frequencies of these *cis* complexes are very similar to those found for the aquo ion.

The pattern of the internal vibrations of the methyl groups also supports a *cis* assignment. For a dimethyl ion, there are two normal modes which involve predominantly symmetrical deformations of the two methyl groups, one in-phase and one out-of-phase vibration. For the *trans* configuration and assuming freely rotating methyl groups, the out-of-phase vibration destroys the effective center of symmetry, and hence should be Raman inactive. In addition, since little coupling would be expected through the heavy metal atom, these would be expected to have very similar frequencies. For the *cis* structure, both vibrations should be Raman active (symmetry species A_1 and B_2, respectively, effective point C_{2v}), and nonbonded interactions resulting from the anticipated 90° C–Au–C angle might be expected to cause slightly different vibrational frequencies. One vibration (A_1) should give a polarized line and the other (B_2) a depolarized line. The spectra of the complexes with the *cis* configuration as well as the aquo ion all show two Raman shifts between 1188 and 1260 cm^{-1} with a separation of 30–40 cm^{-1}. The higher frequency vibration which might be expected to be the in-phase vibration gives a strongly polarized line. The lower frequency line is much less strongly polarized, although the experimental ρ value for the perchlorate solution is less than the expected 0.857. Presumably this results from the fact that the intensity is low (see Figure 1) and hence difficult to measure accurately. In $(CH_3)_3Pt^+$, the symmetrical methyl deformations give a depolarized line at 1250 and a polarized line at 1290 cm^{-1} supporting this assignment. It has also been suggested that the infrared band at 1225 cm^{-1} in the spectrum of $[(CH_3)_3PtI]_4$ results from the symmetrical methyl deformation while the band at 1259 cm^{-1} is from a methyl rocking mode.[27] This seems too high for a methyl rocking vibration. An examination of the data for dimethylplatinum(II) compounds shows that there are always two infrared bands in the range 1170 to 1220 cm^{-1} for *cis* compounds, but in the monomethyl compounds there is but one.[28] Unfortunately, it has not been possible to synthesize the *trans* compounds for which only a single line would be expected.

Perhaps the best evidence concerning the symmetrical methyl deformation frequencies comes from an examination of the infrared spectra of compounds containing the $(NH_3)_2Pt^{II}$ moiety which is isoelectronic with $(CH_3)_2Au^{III}$. The *cis* isomers of $(NH_3)_2PtCl_2$, $(NH_3)_2Pt$-

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[25] R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 768 (1964).

[26] D. E. Clegg and J. R. Hall, *Spectrochim. Acta*, **21**, 357 (1965).

[27] M. N. Hoechstetter, *J. Mol. Spectry.*, **13**, 407 (1964).

[28] D. M. Adams, J. Chatt, and B. L. Shaw, *J. Chem. Soc.*, 2047 (1960).

Table V. Comparison of the Vibrational Frequencies of the $(CH_3)_2Au^{III}$, $(CH_3)_2Pt^{II}$, and $(CH_3)_2Tl^{III}$ Moieties with C_{2v} Symmetry

	ν, cm^{-1}								
	CH_3 stretch		CH_3 deformn		CH_3	MC_2 stretch		MC_2	
Compound	Antisym	Sym	Antisym	Sym	rock	Antisym	Sym	deformn	Ref
cis-$(CH_3)_2Aq(aq)^+$	3012	2927	*a*	1260, 1222	876	591	591	274	This work
$(CH_3)_2Au(acac)$	2990	2915, 2813	*b*	2140, 1201	829?	585	585	268	This work
$[(CH_3)_2AuI]_2$	3000	2904, 2802	1400	1220, 1188	800?	*a*	*a*	*c*	This work
$[(CH_3)_2Au(en)]$ I	*b*	*b*	*b*	1250, 1220	*b*	580	580	240	This work
cis-$(CH_3)_2Pt(P(CH_3)_3)_2$	...	... ...	...	1205, 1183	...	525	508	*c*	28
cis-$(CH_3)_2Pt(P(CH_3)_3)_2$	2930	2880, 2810	...	... ...	...	522	510	*c*	31
cis-$(CH_3)_2Pt(P(C_2H_5)_3)_2$	...	... ...	...	1202, 1179	...	526	506	*c*	28
cis-$(CH_3)_2Pt(Et_2P(CH_2)_2$-$PEt_2)$	...	... ...	...	1218, 1199	...	521	512	*c*	28
$(CH_3)_2Tl(aq)^{+\,d}$	3033	2939	1420	1195	569?	...	498	114	14
$(CH_3)_2Tl(acac)$	...	... ...	...	... ...	...	566	482	*c*	24
$(CH_3)_2Tl(acac)$	...	... ...	...	... ...	...	552	498	*c*	33
$[(CH_3)_2Tl(en)]ClO_4$	...	... ...	...	... ...	...	539	485	*c*	33

[a] Intensity too low to be measured [b] Obscured by ligands [c] Beyond range of instrument [d] Effective point group D_{3d} assigned.

Br_2, and $(NH_3)_2PtI_2$ all show two symmetrical ammine deformation frequencies separated by 15–19 cm^{-1}, while the corresponding *trans* isomers show only a single sharp band in this region.[29] Thus, by analogy, the vibrations of $(CH_3)_2Au(aq)^+$ involving methyl deformations strongly indicate the ion has the *cis* structure.

The other internal methyl vibrations are similar to those observed in the heavy metal alkyls. The intensities of the modes involving antisymmetrical methyl deformations are very low in the Raman effect. The broad band at *ca.* 1400 cm^{-1} in the infrared spectrum of $[(CH_3)_2AuI]_2$ is assigned to these vibrations. The strong, polarized line at 2926–2927 cm^{-1} with the aquo ion is assigned to totally symmetrical C–H stretching and the depolarized line at 3012 cm^{-1} to antisymmetrical C–H stretching. In addition a weak band occurs in the infrared spectra at 2813 cm^{-1} with both $[(CH_3)_2AuI]_2$ and $(CH_3)_2Au(acac)$. While it is possible that this is a first overtone of a vibration involving antisymmetrical methyl deformation, no similar frequency was observed in the spectra of methyltin compounds,[20] a line does occur at 2823 cm^{-1} in the Raman spectra of $(CH_3)_3$-$Pt(aq)^+$, and three C–H stretching bands also appear in infrared spectra of $(CH_3)_2Pt^{II}$ compounds.[30] Thus the 2813-cm^{-1} band in the infrared spectra of the dimethylgold(III) compounds is also assigned to C–H stretching, and the splitting of the symmetrical methyl stretch would occur analogously to that of the symmetrical methyl deformation.

While stretching vibrations of the Au–C bonds result in appreciable changes in the aquo-ion polarizability and an intense Raman line, the dipole moment apparently varies little during these vibrations. Repeated attempts to find a band in the infrared spectrum of $[(CH_3)_2AuI]_2$ assignable to Au–C stretching failed. The same effect has been reported by Kettle for $[(CH_3)_3$-$PtCl]_4$[31] and by Hoechstetter for $[(CH_3)_3PtI]_4$.[27] We have also noted this with $(CH_3)_2PbCl_2$ where no band assignable to Pb–C bond stretching could be found in repeated examinations of infrared spectra. These bonds between carbon and metals in the bottom row of the periodic table appear to be rather nonpolar which, perhaps, accounts to some extent for their inertness to substitution. It should be noted, however, that Morgan, *et al.*, report a weak band at 590 and a shoulder at 470 cm^{-1} in infrared spectra of $[(CH_3)_3PtOH]_4$ which they assign to PtC_3 bond stretching.[32]

Vibrational frequencies for the $(CH_3)_2M$ moiety in the *cis*-dimethylgold(III) compounds, several *cis*-dimethylplatinum(II) compounds,[28,30] and some dimethylthallium(II) compounds[24,33] are listed in Table V. The frequencies of the Pt(II) and Au(III) compounds are quite similar with the expected increase in the M–C_2 stretching frequency with metal valence on going from divalent platinum to trivalent gold. Surprisingly, both symmetrical and antisymmetrical Pt^{II}–C_2 stretching frequencies differing by 10–20 cm^{-1} have been reported, while these appear to be degenerate in the gold(III) and Pt(IV) compounds. Apparently no Raman studies have been made of any of the Pt(II) compounds.

Thallium–carbon stretching vibrations have been reported for several compounds where the four bonds about thallium are presumably directed toward tetrahedral vertices. The frequencies of the symmetrical M–C_2 vibrations of the gold(III) compounds are considerably higher than for the thallium(III) compounds indicating, qualitatively, the effect of the d orbital contribution in strengthening the metal–carbon bonds.

The transition metal ion $(CH_3)_2Au^+$ provides an interesting contrast to the nontransition metal ions $(CH_3)_2Tl^+$, $(CH_3)_2Sn^{2+}$, and $(CH_3)_2Pb^{2+}$. The former adopts the *cis* angular configuration, while the latter ions have been assigned structures with 180° C–M–C bond angles. The primary difference in their behavior in aqueous solutions is that the dimethylgold(III) ion forms much more covalent bonds to water molecules in the first coordination sphere than the nontransition metal species as judged from the high Raman intensity of the Au–O stretch. In this respect, $(CH_3)_2Au^{III}$ is more like $(CH_3)_2Ge^{IV}$ which exists even in strongly acidic solutions as $(CH_3)_2Ge(OH)_2$ with an angular C–Ge–C skeleton. When interactions with coordinated water are highly polar and hence not strongly

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

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directional in character, the stereochemistry of the ion is probably determined by the configuration minimizing the energy of the $(CH_3)_2M$ moiety.[17]

The fact that $(CH_3)_2Au^+$ seems to exist exclusively as the *cis* ion may indicate a strong *trans* effect associated with the methyl groups. Similarly, synthesis of dimethylplatinum(II) compounds always seems to give the *cis* isomer.

Hyperfiltration Studies. IV. Salt Rejection by Dynamically Formed Hydrous Oxide Membranes[1]

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Abstract: Salt-filtering layers can be formed on porous bodies (pore diameters as large as 5 μ) by circulating by them under pressure solutions containing colloidal dispersions of hydrous oxides or solutions of hydrolyzable salts. These films reject substantial fractions of solute from dilute solutions, frequently with transmission rates through the membranes as high as 1 cm/min (35 atm).

In a canvass of materials for possible usefulness as salt filters in the hyperfiltration, or reverse osmosis, process for desalination, hydrous oxides and basic salts deserve consideration. These materials are known to have ion-exchange properties,[3] and ion-exchange membranes and porous bodies are known to reject salt from solutions[4-8] forced through them by pressure. It is not obvious, however, how to prepare a hydrous oxide layer suitable for hyperfiltration. In order to reject, it must be compact enough for intimate contact with feed;[5] at the same time, it must be thin enough to allow fast permeation (as the "active layer" of presently prepared cellulose acetate membranes does).[9]

We have found that "membranes" can be dynamically created by exposing a porous body mounted in a hyperfiltration apparatus to a solution containing a colloidal dispersion of a hydrous oxide. A hyperfiltration apparatus consists of a membrane and support in contact with a pressurized feed solution; the solution is circulated past the membrane to decrease the salt buildup resulting from rejection of solute from the solution permeating the membrane.[10] The equipment used in this study differed from that previously described[6] in that a large volume of solution was pressurized, and circulation was effected with a separate pump operating at pressure.

In a typical example, enough of a 0.1 M $FeCl_3$ solution, which had been aggregated by having been brought to a boil, was added to a 0.02 M NaCl solution to make it 0.0005 M in Fe(III); the sodium chloride solution was circulating in the hyperfiltration apparatus past a silver frit of 0.8-μ average pore size.[11] The initially fast permeation rate rapidly dropped to 0.2 cm min^{-1} (1 cm/min = 354 U. S. gal day^{-1} ft^{-2}) at 35 atm, and salt rejection, $\mathbf{R}_{obsd} = (c_f - c_\omega)/c_f$, based on total chloride, rose to 0.6. The symbol c refers to concentration in moles/liter, subscript f refers to the feed solution, and ω refers to the solution effluent from the membrane.

Results of a more extended experiment are given in Table I. A 0.25 M $ZrOCl_2$ solution was boiled for several hours, until formation of a suspension was barely perceptible, and enough of this solution was added to the feed to bring it to the additive concentrations shown in the table. The initial exposure of the 0.8-μ silver frit to a solution 0.02 M in NaCl containing 0.001 M Zr(IV) additive resulted in formation of a rejecting layer; the rejection properties of the membrane decayed only slowly when the experiment was continued without the presence of Zr(IV). The slow decrease could be arrested or reversed by addition of 10^{-4} M Zr(IV) to the feed. Even with the high circulation rates possible with our present apparatus (residence time of solution in contact with membrane about 0.01 sec), concentration polarization is not eliminated at these high permeation rates (around 350 gal day^{-1} ft^{-2}); lower rejections were obtained when the circulation was decreased from the maximum. The rejections given are thus not the maximum possible

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[1] (a) Research sponsored by The Office of Saline Water, U. S. Department of the Interior, under Union Carbide Corporation's contract with the U. S. Atomic Energy Comission. (b) Previous paper in series: J. R. Kuppers, N. Harrison, and J. S. Johnson, *J. Appl. Polymer Sci.*, 10, 969 (1966).

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[11] Obtained from the Selas Flotronics Co. Pore sizes are nominal values of diameter specified by the manufacturer; frit thickness, 40 μ.