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Dimethylgold(III) Halides and Pseudohalides. Reactions, Raman, Infrared, and Proton Magnetic Resonance Spectra, and Structure[1]

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The infrared and Raman spectra of the binuclear molecules $[(CH_3)_2AuX]_2$, X = Cl, Br, I, with effective D_{2h} symmetry have been determined and are compared with the spectra of the anions $(CH_3)_2AuX_2^-$, X = Cl, Br, studied earlier. The stretching frequencies of corresponding ions and molecules are very similar. Even the highest frequency Au–X stretching vibrations of the bridges are only *ca.* 5% lower than the terminal Au–X stretches of the corresponding $(CH_3)_2AuX_2^-$ anions, although the bridge stretching frequencies of $[(CH_3)_2AuCl]_2$ appear to be about 20% lower than the corresponding vibrations of $[AuCl_3]_2$. The intensities of these Raman bands increase in the sequence $Cl \ll Br < I$, while the Au–C_2 stretching frequencies decrease in the same order. Both observations suggest increasing covalency in the gold–halogen bridges with the heavier halogens. Dimethylgold(III) thiocyanate was synthesized and assigned a centric C_{2h} structure on the basis of proton magnetic resonance and vibrational spectra. Thiocyanate bridges *via* both the nitrogen and the sulfur atoms. Thiourea cleaves the bridge giving a molecule with sulfur-bonded thiourea and a sulfur-bonded, terminal thiocyanate. The dimethylgold(III) moiety is stabilized by a wide variety of ligands ranging from OH^- to S, P, and As donors in contrast to the isoelectronic dimethylplatinum moiety which is stabilized only by the heavier donor atoms.

Introduction

The dialkylgold(III) moieties form a number of stable compounds with uninegative ligands. Since the typical square-planar coordination expected for d^8 gold(III) normally is found, the anions are forced to bridge gold atoms, and the products are polymeric, $[R_2AuX]_n$. With X = Cl, Br, and I, dimers are formed, and an early X-ray structure determination[5] confirms the square-planar coordination about gold in $[(C_2H_5)_2AuBr]_2$.

An analogous structure with oxygen bridges was proposed for trimethylsiloxydimethylgold(III) which is dimeric in benzene.[6] With dimethylgold(III) hydroxide, a binuclear complex exists in dilute aqueous solution (2.4 m*M*),[7] but the solid compound isolated is $[(CH_3)_2AuOH]_4$ with a puckered eight-membered ring.[8] This structure should lead to longer gold–gold interactions, and an analogous one would be expected for the fluoride.

Sulfur-containing ligands seem to give stable binuclear complexes, and a di-μ-mercapto structure is indicated for dimethylgold(III) thiophenolate.[9] Gent and Gibson[10] reported that diethylgold(III) thiocyanate was dimeric in benzene solution, and a sulfur-bridged structure was assigned by analogy with the mercaptides. Also, it was reported that nitrogen bases would not cleave the bridge, and this suggested sulfur bridging.

Recently, dimeric dimethylgold(III) azide was prepared by Beck, *et al.*[11] A structure with D_{2h} symmetry was assigned on the basis of the infrared and pmr spectra, and this has been confirmed by an X-ray structure determination.[12] Each azide bridges through one nitrogen atom only.

As part of a study on organogold(III) stereochemistry, the infrared, Raman, and proton magnetic resonance spectra of several dimethylgold(III) halides and pseudohalides have been determined, and some reactions of these compounds have been studied. Some time ago, we reported detailed infrared spectra for $[(CH_3)_2AuI]_2$.[13] At that time, only mercury arc excitation was available to excite the Raman spectrum, and the 4358-Å radiation photolyzed the compound. In this work, an He–Ne laser was employed, and there was no decomposition of the samples.

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 Gibson.[14] Molecular weights were determined with a Hewlett-Packard Model 302 vapor pressure osmometer using benzil–CCl_4 solutions for calibration. Melting points were observed with a Fisher-Johns apparatus.

Di-μ-chloro-tetramethyldigold(III), Di-μ-bromo-tetramethyldigold(III), and Centric Di-μ-thiocyanato-*S*,*N*-tetramethyldigold(III).—Di-μ-iodo-tetramethyldigold(III) (0.84 g, 2.4×10^{-3} mol) was dissolved in hexane, and acidified 0.2 *M* $AgNO_3$ (12.0 ml, 0.5 *M* in HNO_3) was added dropwise. To ensure completion of reaction 1, the two layers were stirred for 2 hr and then separated. To the aqueous phase was added a solution of NaX (2.5×10^{-3} mol), and the precipitate of $[(CH_3)_2AuX]_2$ was collected on a frit. Yields of greater than 95% could be obtained by extracting the aqueous phase with 30-ml portions of CCl_4. After stirring for 15 min, the layers were separated, the CCl_4

$$[(CH_3)_2AuI]_{2(hexane)} + 2Ag^+_{(aq)} \longrightarrow 2(CH_3)_2Au^+_{(aq)} + \underline{2AgI} \quad (1)$$

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TABLE I

INFRARED AND RAMAN SPECTRA OF $[(CH_3)_2AuX]_2$ (X = Cl, Br, I, NCS)[h]

$\nu[(CH_3)_2AuCl]_2$, cm^{-1}, Ir			$\nu[(CH_3)_2AuBr]_2$, cm^{-1}		$\nu[(CH_3)_2AuI]_2$, cm^{-1}		$\nu[(CH_3)_2AuNCS]_2$, cm^{-1}, Ir			
Soln[a]	Mull	Raman[e]	Ir[c]	Raman[f]	Ir	Raman[e]	Soln[b]	Mull	Raman[g]	Qualitative assignments
3009 m	3003 w		3000 2955		3000 w, b		3000 w	3000 w		$\nu_{as}(CH_3)$
2919 s	2913 m	2915 m	2908	*d*	2904	*d*	2913 m	2914 m	2910 m	$\nu_s(CH_3)$
	2864				2813					$2\delta_{as}(CH_3)$
								2163 m	2151 m	$\nu(C\equiv N)$
	1413 m		1405		1400 w			1412 w		$\delta_{as}(CH_3)$
1213 s	1229 1219	1241 w	1229	1232 m	1220 m	1222 m	1239 s	1239 s	1239 w	$\delta_s(CH_3)$
1199 vs	1202 w 1192 m 1187 s	1199 m	1198	1193 m	1188 m	1181 m	1196 vs	1195 vs	1195 m	
818 m	830 m		810		800 w			816 w		$\rho_r(CH_3)$
								775 m		$\nu(C—S)$
	550 w	571 p 561 vs	530 (?)	561 550 vs		550 p 545 vs		548 w	577 p 548 vs	$\nu(Au—C)$
									444 w 430 vw, sh	$\delta(NCS)$, $\nu(Au—N)$
		289 vw, sh		266 m		. . .			276	$\delta(CAuC)$
	256 vs	273 m		181 vs		141 131 s			239 s 194 m	$\nu(Au_2X_4)$
		154 b		149 b						

[a] CS_2 solution, 4.5 m*M*. [b] CS_2 solution, 50 m*M*. [c] Data from ref 6. [d] Region obscured by Lyman ghost. [e] Recorded both with a crystalline powder sample and with a saturated petroleum ether (bp 60–68°) solution. [f] Crystal powder spectrum. [g] Recorded both with a crystalline powder sample and with a saturated CCl_4 solution. [h] Abbreviations: s, strong; m, medium; w, weak; v, very; b broad; p, polarized.

phase was evaporated, and the white, crystalline product remained. The compounds were recrystallized from *n*-hexane and dried over P_4O_{10} under vacuum at 5°. *Anal.* Calcd for C_2H_6ClAu: C, 9.40; H, 2.42; Cl, 13.4; Au, 74.8. Found: C, 9.16; H, 2.30; Cl, 13.5; Au, 75.0; mp 72–73°. Mol wt: calcd for a dimer, 524; found, in benzene, 0.039 *M*, 503 amu. The melting point of $[(CH_3)_2AuBr]_2$ was 68°; lit.[6] mp 68°. *Anal.* Calcd for C_3H_6NSAu: C, 12.8; H, 2.26; N, 4.97; S, 11.52; Au, 69.2. Found: C, 12.6; H, 2.12; N, 4.91; S, 11.2; Au, 69.1; mp 73–74°. Mol wt: calcd for a dimer, 570; found, in CCl_4, 0.0108 *M*, 647 amu; 0.0207 *M*, 602 amu.

Dimethylthiocyanatothioureagold(III).—To a solution of $[(CH_3)_2AuNCS]_2$ (0.52 g, 1.8 × 10^{-3} mol) in $CHCl_3$–*n*-hexane was added an aqueous solution of thiourea (0.15 g, 5 × 10^{-3} mol). The white precipitate which formed was collected on a frit, washed with $CHCl_3$ and water, and recrystallized from H_2O–acetone; yield 0.52 g, 80%. *Anal.* Calcd for $C_4H_{10}N_3S_2Au$: C, 12.9; H, 2.71; N, 11.3; S, 17.3; Au, 53.1. Found: C, 13.6; H, 2.86; N, 11.5; S, 17.5; Au, 54.2; mp 83°.

Raman Spectra.—These were obtained with an instrument built around a Spex Model 1400 double monochromator, and a Spectra Physics Model 112 He–Ne laser (6328 Å) producing in excess of 30 mW was used to excite the spectra. The signal was detected with a cooled (−85°) EMI 9558A photomultiplier. In early experiments, the laser beam was chopped, and the signal was amplified with a Princeton Applied Research CR-4 preamplifier and a JB-4 lock-in amplifier. Later spectra were obtained using a Keithley Model 417 picoammeter for detection of high-level signals and Canberra counting equipment for low-level signals. The instrument was calibrated with a mercury arc, the 6328-Å laser line, and carbon tetrachloride. Solution spectra were obtained with capillaries containing up to *ca.* 50 μl of solution. Powder spectra were obtained either by 90° illumination of a thin layer of the compound or by the transillumination technique in a thin capillary tube. Because of the rather intense ghosts of the 1200 grooves/mm (7500-Å blaze) Bausch and Lomb gratings used in the monochromator, it was not possible to obtain meaningful powder spectra at shifts of less than 90 cm^{-1} from the exciting line. Frequencies of sharp lines are accurate to ±2 cm^{-1}. In one experiment, a Cary laser 81 spectrophotometer was used.[15]

Infrared Spectra.—Infrared spectra were recorded on either a Perkin-Elmer 521 or a Beckman IR-12 spectrometer. Spectra of solids were obtained as split mulls. Instrument calibration was effected with polystyrene film and neat indene. The frequencies of sharp bands are accurate to ±2 cm^{-1}, while those for broad bands are within ±5 cm^{-1}. A far-infrared spectrum for $[(CH_3)_2AuCl]_2$ was run on a Beckman IR-11 spectrometer as a Nujol suspension between polyethylene windows.[16]

Proton Magnetic Resonance Spectra.—Spectra were recorded with Varian A-60 and A-60D spectrometers at *ca.* 40°. Coupling constants were measured using side bands and are believed to be accurate to ±0.5 Hz.

Data and Results

Assignment of the Spectra of the $[(CH_3)_2AuX]_2$ Molecules (X = Cl, Br, I).—The data for these molecules are collected in Table I. The Raman spectra are illustrated in Figure 1, while Figure 2 shows the infrared spectrum of the chloride. Several studies have been made of planar halogen-bridged molecules and ions of the M_2X_6 type with symmetry D_{2h}. Raman and infrared spectra have been reported for $[AuCl_3]_2$,[17–19] $[ICl_3]_2$,[19,20] and the ions $[MX_3]_2^{2-}$ (M = Pd(II), Pt(II); X = Cl, Br, I).[21] In solid $[(CH_3)_2AuI]_2$, the methyl groups appear to be freely rotating at room temperature with a barrier estimated as 270 ± 70 cm^{-1}.[22] Consequently, the effective symmetry of the $[(CH_3)_2AuX]_2$ molecules is taken as D_{2h}. As expected, normal-coordinate calculations on the $(CH_3)_2AuX_2^-$ ions (X = Cl, Br) indicated that there is minimal coupling between the internal methyl and skeletal vibrations.[23]

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[15] This spectrum was 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 this spectrum.

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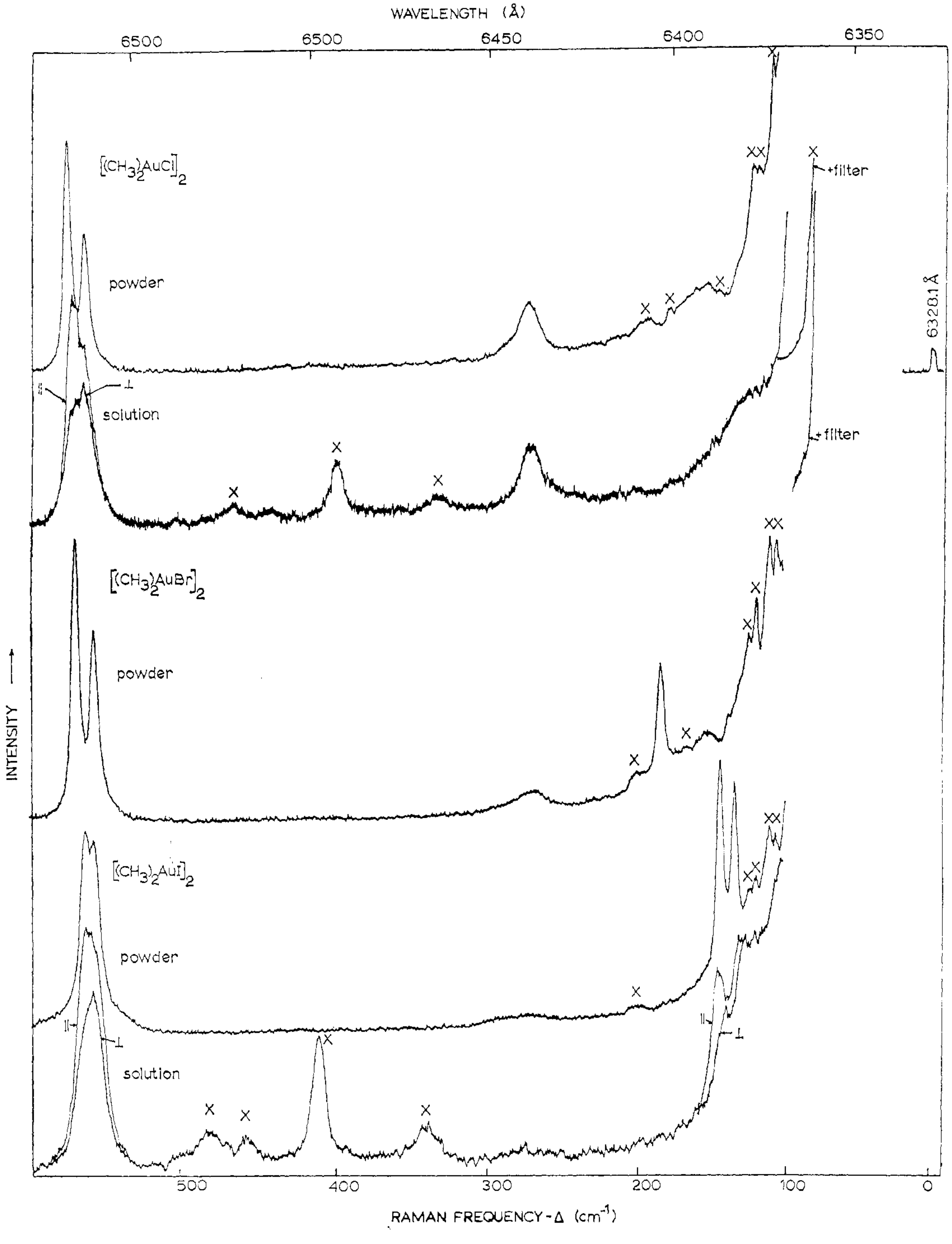


Figure 1.—Laser Raman spectra of $[(CH_3)_2AuX]_2$ molecules, X = Cl, Br, I. The spectra were recorded with microcrystalline powders and solutions in petroleum ether. Grating ghosts are marked with X. The powdered compounds are very effective diffuse scatterers and give very intense ghosts. Scattering from the solvent (petroleum ether, bp 60–68°) is also marked with X. Slits are *ca.* 0.5 Å (1.2 cm^{-1}).

That this is also the case with the $[(CH_3)_2AuX]_2$ molecules is borne out by examination of the data in Table I which show only very small variations from one molecule to another in the frequencies involving the C–H and H–C–H internal coordinates. Consequently, only the skeletal modes of the $[(CH_3)_2AuX]_2$ molecules will be considered here. The doubling of the $\delta_s(CH_3)$ bands in the 1200–1300-cm^{-1} region of the infrared spectrum of the crystalline chloride, Figure 2, indicates weak interactions of the molecules in the unit cell.

The representation for the normal skeletal modes is $\Gamma = 4\ a_g + 3\ b_{1g} + b_{2g} + b_{3g} + a_u + 2\ b_{1u} + 3\ b_{2u} + 3\ b_{3u}$. The nine even modes are Raman active, the a_u mode is inactive, and the eight other odd modes are infrared active. The in-plane vibrations belong to species a_g, b_{1g}, b_{2u}, and b_{3u} (molecular plane = σ_{xy}). Many of these skeletal frequencies also are very similar

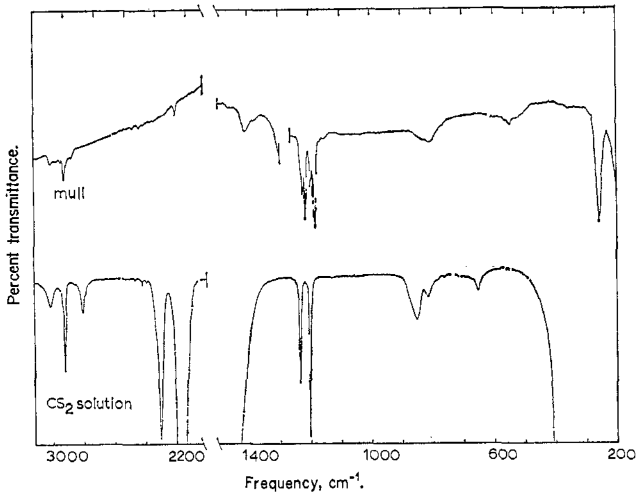


Figure 2.—Infrared spectrum of $[(CH_3)_2AuCl]_2$. This spectrum was recorded with a split mull and a CS_2 solution.

to those of the $(CH_3)_2AuX_2^-$ anions and can be assigned on this basis.

Au–C Stretching ($a_g + b_{1g} + b_{2u} + b_{3u}$).—The AuC_2 stretching frequencies of $(CH_3)_2AuCl_2^-$ were observed at 563 and 572 cm^{-1}, and the corresponding Raman-active vibrations ($a_g + b_{1g}$) of $[(CH_3)_2AuCl]_2$ are assigned at 571 and at 561 cm^{-1}, respectively. The AuC stretching vibrations give very weak infrared bands in all of these compounds, and often these cannot be assigned with any confidence from an infrared spectrum. Coupling of the AuC coordinates is even less with the bromide and iodide, and these compounds give intense Raman scattering at 550, 561 and 545, 550 cm^{-1}, respectively. Polarization measurements for solutions of the chloride and iodide show that the higher frequency Raman-active vibration is of species a_{1g}.

C–Au–C Deformation ($a_g + b_{3u}$).—These frequencies are very similar to those of the $(CH_3)_2AuX_2^-$ anions and in the Raman spectra (a_g mode) are assigned at 289, 266, and *ca.* 260 cm^{-1} for the chloride, bromide, and iodide, respectively. In the case of $[(CH_3)_2AuCl]_2$, there is probably some mixing of this C–Au–C internal coordinate with the stretching coordinate in the two vibrations observed in this region. This also is suggested by the decrease in intensity of this vibration from chloride to iodide. These bending vibrations have not been observed in the infrared spectra of any of the dimethylgold(III) compounds.

Au–X Stretching ($a_g + b_{1g} + b_{2u} + b_{3u}$).—Surprisingly, the highest frequency Raman-active Au–X stretching frequencies of the $[(CH_3)_2AuX]_2$ molecules are very similar to the values found for the $(CH_3)_2AuX_2^-$ anions. For $(CH_3)_2AuCl_2^-$, two Raman frequencies were observed at 281 (ν_s) and 268 (ν_{as}) cm^{-1}, while the broad band at 273 cm^{-1} with $[(CH_3)_2AuCl]_2$ is assigned to the ($a_g + b_{1g}$) Au_2Cl_4 modes of the bridge. The corresponding Raman values for the dibromo anion were 197 and 179 cm^{-1}, and $[(CH_3)_2AuBr]_2$ has an intense band at 181 cm^{-1}. The infrared spectrum of $[(CH_3)_2AuCl]_2$ shows a broad band centered at *ca.* 256 cm^{-1} which appears to consist of a band at 273 cm^{-1} and a much broader, overlapping band centered at *ca.* 245 cm^{-1}, and these are assigned to the b_{2u} and b_{3u} modes. As noted above, it is likely that the C–Au–C deformation will couple somewhat with the Au–Cl bridge stretching in the normal modes observed between 250 and 300 cm^{-1}. The Au–I stretches give two very intense Raman bands at 131 and 141 cm^{-1}. Only the higher frequency band is well separated from the background in the solution spectrum, it is clearly polarized, and it is assigned to the a_{1g} mode.

C–Au–X and X–Au–X Deformations.—The former are of symmetry species $a_g + b_{1g} + b_{2u} + b_{3u}$, but there are a_g and b_{3u} redundancies in the angles about gold. Similarly the X–Au–X coordinates transform as $a_g + b_{2u}$, but there is a b_{2u} redundancy involving these angles. It might be expected that the normal-coordinate calculations on Au_2Cl_6[17-19] would be of help, at least in identifying the a_g ring stretch and deformation. Unfortunately, the assignments made for the low-frequency vibrations are quite different. For example, Adams and Churchill[17] and Forneris, *et al.*,[19] assigned the a_g ring deformation at 99 (96) cm^{-1}, while Beattie, *et al.*,[18] assigned the same band (97 cm^{-1}) to a b_{1g} rocking mode of the terminal chlorines. They calculated values of 55–64 cm^{-1} for the a_g ring mode. No attempt will be made here to assign these low-frequency bending modes or the out-of-plane deformations. Only a very broad, weak band below 150 cm^{-1} was observed which could be assigned to these modes. Otherwise only weak grating ghosts were found in this region.

Proton Magnetic Resonance Data.—Data for the three halides, the thiocyanate, and the bis(dimethyl sulfide) complex cation[23] are given in Table II. The D_{2h} molecules give a single sharp resonance. The methyl proton τ values of the halides occur in the same order as for the $(CH_3)_2AuX_2^-$ anions although they are shifted *ca.* 0.1–0.2 ppm farther upfield with the anions.

TABLE II

PROTON MAGNETIC RESONANCE DATA ON DIMETHYLGOLD(III) COMPOUNDS

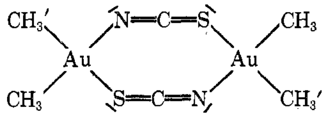
Compound	Solvent	τ,[a] ppm	$^1J(^{13}C-^1H)$, Hz
$[(CH_3)_2AuCl]_2$	CCl_4	8.72	141.7
$[(CH_3)_2AuBr]_2$	CCl_4	8.62[b]	142.3
$[(CH_3)_2AuI]_2$	CCl_4	8.49	142.5
$[(CH_3)_2Au(SCN)]_2$	$CHCl_3$	8.70 (1)[c] 9.05 (1)	. . .
$[(CH_3)_2Au[S(CH_3)_2]_2]Cl$	H_2O	8.72 (1) 7.43 (2)[d]	140.5

[a] TMS or trimethylsilyl propanesulfonate (aqueous solution) = 10. [b] Lit.[6] value 8.63 ppm. [c] Relative intensities in parentheses. [d] Dimethyl sulfide protons.

Dimethylgold(III) Thiocyanate.—This compound was found to be dimeric in CCl_4 in agreement with Gent and Gibson's[10] observations on the diethyl compound in benzene. The pmr spectrum in chloroform exhibited two sharp resonances with equal intensities at τ 8.70, 9.05 ppm. This rules out the symmetric

D_{2h} structure with sulfur bridges suggested by Gent and Gibson.

Four structures which would lead to two sets of six symmetrically equivalent protons each per dimer are I–IV. Thiocyanate shows little evidence of adopting an electron distribution corresponding to the N=C=S canonical structure, and this favors structure IV. Structure III can be eliminated on the basis of the infrared and Raman spectra. Since one CN group is intimately associated with the ring while the other is not, two very different C≡N stretching frequencies should result. The observed frequencies differ by only 12 cm^{-1}. The structure also is unlikely because of the difference in size and donor ability of sulfur and nitrogen. The vibrational spectra are in accord with structure IV. These are given in Table I and are illustrated in Figures 3 and 4.



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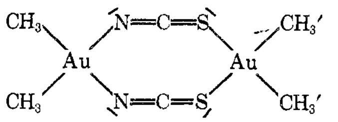

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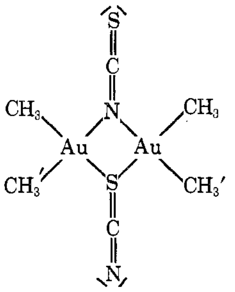

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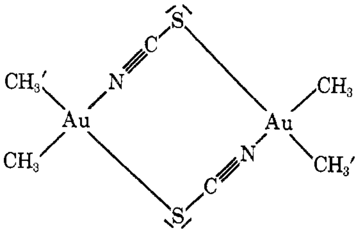

IV

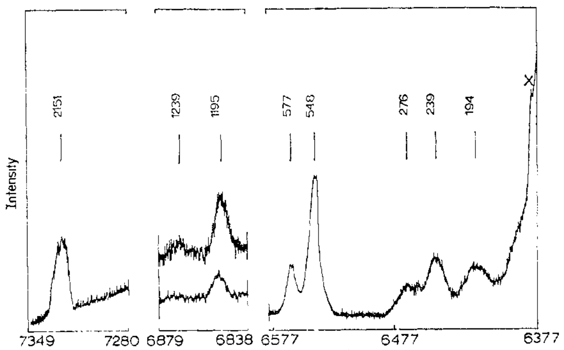

Figure 3.—Raman spectrum of $[(CH_3)_2AuNCS]_2$. The sample was a crystalline powder. The grating ghost is marked with ×, and the Raman shifts are in cm^{-1}.

The symmetry of IV is C_{2h}. The four Au–C coordinates transform as 2 a$_g$ + 2 b$_u$, the former being Raman and the latter infrared active. Two vibrations are observed in the Raman spectrum at 577 and 548 cm^{-1}. Both were found to be polarized from measurements with a saturated CCl$_4$ solution using a Cary laser 81, consistent with their assignment. Because of the very low intensity of the vibrations in the infrared spectrum, only one very weak band could be detected. For this structure, the (C≡N) coordinates transform as a$_g$ + b$_u$. Only one Raman-active vibration was observed at 2151 cm^{-1}, although it is rather broad in the crystal spectrum, and only one infrared band was found at 2163 cm^{-1} strongly supporting the centrosymmetric structure. The high frequencies are consistent with the bridging structure involving both nitrogen and sulfur coordination.[24]

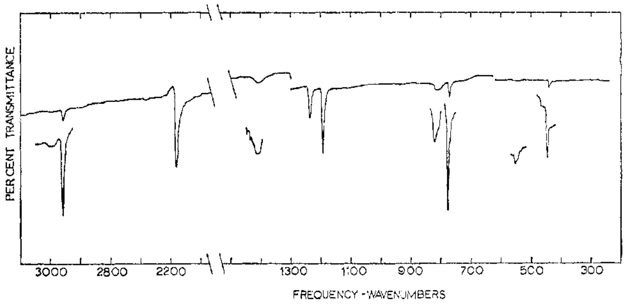

Figure 4.—Split mull infrared spectrum of $[(CH_3)_2AuNCS]_2$.

The divalent platinum complex $Pt_2(SCN)_2Cl_2(P(C_3H_7)_3)_2$ exists in two isomers both of which have been shown by X-ray diffraction[25] to have the type of bridge proposed in IV. Unusually high infrared-active (C≡N) stretching frequencies similar to that of $[(CH_3)_2AuNCS]_2$ also were observed for the cis and trans isomers of the platinum complex, 2162 and 2169 cm^{-1}, respectively.

The appreciable separation of the two a$_g$ Au–C stretching modes suggests that the lower frequency (548 cm^{-1}) involves primarily the stretching of bonds trans to sulfur, while the higher frequency (577 cm^{-1}) mainly involves the bonds trans to nitrogen. Because of the orthogonal nature of these internal coordinates, coupling *via* the kinetic energy terms should be a minimum. For comparison, the totally symmetric AuC stretch of $(CH_3)_2Au[S(CH_3)_2]_2^+$ occurs at 552 cm^{-1}.[23]

Dimethylthiocyanatothioureagold(III).—The charge-reducing effect of the two methide ligands bound to Au(III) can be seen in the stability of $(CH_3)_2Au(NCS)SC(NH_2)_2$. Reaction of thiourea with inorganic Au(III) compounds leads to reduction of the gold.[26] The spectra of this compound are tabulated in Table III. They indicate coordination *via* the sulfur atom both of thiourea and of thiocyanate. The N–H stretching frequencies of the complex are slightly higher than for free thiourea suggesting S coordination.[27] The band at 480 cm^{-1} also is characteristic of sulfur-bonded thiourea and has been assigned to an N–C–N deformation.[26,27]

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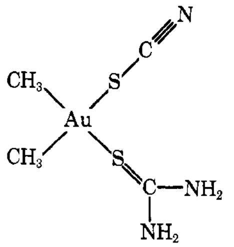
TABLE III

INFRARED AND RAMAN SPECTRA OF cis-$(CH_3)_2Au(SCN)(SC(NH_2)_2)$

ν, cm^{-1}		
Infrared	Raman	Qualitative assignments
3409 m, b		$\nu(NH_2)$
3295 m, b		
3194 m		$2\delta(NH_2)$
3000 w, b		$\nu_{as}(CH_3)$
2918 m	a	$\nu_s(CH_3)$
2903 sh		
2119 s	2117 vs	$\nu(C{\equiv}N)$
1623 s		$\delta(NH_2)$
1604 s		
1476 w		$\rho(C—NH_2)$, $\nu(N—C)$, $\nu(C{=}S)$
1457 m		
1409 s		
1223 s		$\delta_s(CH_3)$
1190 s		
~1050 vw		$\rho(C—NH_2)$, $\nu(N—C)$, $\nu(C{=}S)$
791 s, b		$\rho_r(Au—CH_3)$
	723 m	$\nu(C—S)$
543 m	554 vvs	$\nu(AuC_2)$
	546 vs	
480 m	480 m	$\delta(NCN)$, $\delta(NCS)$
430 s		$\delta(NCS)$
	281	$\delta(CAuC)$
	255	$\nu(Au—S)$

[a] Obscured by Lyman ghost.

The frequencies assigned to the thiocyanate group also suggest sulfur bonding.[28,29] Coordination of thiourea to $[(CH_3)_2AuNCS]_2$ reduces the (C≡N) stretching frequency from 2163 (ir), 2151 (R) to 2119 (ir), 2117 (R) cm^{-1}, values typical for a sulfur-bonded, terminal thiocyanate.[30,31] With $[(C_2H_5)_4N][Au(SCN)_4]$[31] an infrared band is observed at 2127 cm^{-1}. The band in the Raman spectrum of $(CH_3)_2Au(SCN)(SC(NH_2)_2)$ at 723 cm^{-1} is assigned to C–S stretching and is typical for a sulfur-bonded thiocyanate[28,32] ($[(C_2H_5)_4N][Au(SCN)_4]$), 695 cm^{-1} from infrared)[31] as is the N-C-S deformation at 430 cm^{-1} ($[(C_2H_5)_4N][Au(SCN)_4]$, 415, 454 cm^{-1}). These data are consistent only with the structure



V

The frequency of the thiocyanate C–S stretch has been reported to provide one of the better criteria for assigning the mode of thiocyanate coordination. Its application has been limited, however, by the low infrared intensity of C–S stretching vibrations. Fortunately this group vibration seems to have a rather high Raman intensity consistent with C–S stretches in sulfonate ions[33] and dimethyl sulfide.[23]

The characteristically intense AuC_2 stretches are observed at 546 and 554 cm^{-1} compared to 548 and 577 cm^{-1} for $[(CH_3)_2AuNCS]_2$ where one bond is trans to sulfur and one to nitrogen. The average of the AuC_2 stretches for $(CH_3)_2Au(SCN)(SC(NH_2)_2)$ is very similar to the value for $[(CH_3)_2AuI]_2$. The Au–S stretching vibrations should give intense Raman scattering, and the line at 255 cm^{-1} is assigned to one of these.

Discussion

The binuclear diorganogold(III) halides have been known since the beginning of the century and they provide particularly simple examples of di-μ-halogeno-bridged complexes. The Au–C stretching frequencies show the same trend with the trans ligand as found for the dihalogeno anions (average of Raman-active vibrations): $[(CH_3)_2AuX]_2$: 566, 558, 547; X = Cl, Br, I; cis-$(CH_3)_2AuX_2^-$: 572, 558; X = Cl, Br. In the force constant calculations for the anions,[23] it was determined that the least polarizable X ligands lead to the strongest gold–carbon bonds.

The internal methyl vibrations of these molecules should hardly couple with the skeletal modes, so a comparison of $[(CH_3)_2AuCl]_2$ with $[AuCl_3]_2$ is of interest, because they have the same D_{2h} skeletal symmetry. With the dimethyl compound, the terminal and bridge skeletal stretches should be coupled to a much lesser extent than for auric chloride. Three detailed studies on $[AuCl_3]_2$ have been carried out recently including normal-coordinate analyses.[17-19] Unfortunately, although all of the calculations reproduce the experimental frequencies well, very different assignments of the frequencies were made. For example, Adams and Churchill[17] and Beattie, *et al.*,[18] agreed on the assignment of only two out of nine Raman bands. For the observed infrared vibrations, the agreement is somewhat better. In a comparison of $AuCl_4^-$ and $(CH_3)_2AuCl_2^-$ it was found that the trans methyl groups led to a decrease of 19% in the totally symmetric Au–Cl stretching frequencies. Applying the same figure to the average value of the a_g Au–Cl bridge stretch of Au_2Cl_6 taken from ref 17 and 18, an estimate of 267 cm^{-1} is obtained for the Au–Cl bridge stretch of $[(CH_3)_2AuCl]_2$. A value of 273 cm^{-1} was assigned in the spectrum. The trans bond weakening effect of the methyl ligands is very similar in both the binuclear molecules and anionic complexes.

The similarity of the totally symmetric Au–Cl bridge stretching frequency of $[(CH_3)_2AuCl]_2$, 273 cm^{-1}, to the a_1 terminal stretching frequency of $(CH_3)_2AuCl_2^-$, 281 cm^{-1},[23] is unusual. It seems very likely that the Au–Cl stretching force constant will be lower for the bridge. On the other hand, the bridge stretching vibration involves two Au–Cl internal coordinates, and this will tend to compensate for the effect of the de-

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[28] For a general discussion of the vibrations of coordinated thiocyanate and isothiocyanate, see D. M. Adams, "Metal Ligand and Related Vibrations," Edward Arnold, London, 1967, pp 277, 318.

[29] The ambidentate nature of thiocyanate and its mode of coordination have been discussed by J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966); **3**, 225 (1968).

[30] A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 1665 (1965).

[31] A. Sabatini and I. Bertini, *ibid.*, **4**, 959 (1965).

[32] M. E. Farogo and J. M. James, *ibid.*, **4**, 1706 (1965).

[33] M. G. Miles, G. Doyle, R. P. Cooney, and R. S. Tobias, *Spectrochim. Acta, Sect. A*, **25**, 1515 (1969).

crease in the AuCl stretching force constant on the frequency.

With the dimeric halides, a broad band was observed at *ca.* 150 cm^{-1}. By analogy with Au_2Cl_6, it might be expected that out-of-plane bending vibrations would occur in this region. Because of the uncertainty of the assignment of the low-frequency modes and complications arising out of the redundancies in the angles about gold and in the bridge, no further analysis of the low-frequency data was attempted.

In contrast to the isoelectronic dimethylplatinum(II) moiety the dimethylgold(III) group can be stabilized with a very wide range of ligands. In general the trends in the metal–carbon and metal–X bond strengths are the same as observed for methylmercury(II) compounds.[34]

The thiocyanate $[(CH_3)_2Au(NCS)]_2$ is particularly unreactive, and this must be associated with the di-μ-thiocyanato-*N,S* bridge. Foss and Gibson[35] found that these diorganogold(III) thiocyanates were not attacked by nitrogen bases, *e.g.*, ethylenediamine, which cleaves the chloride, bromide, and iodide.[36] Sulfur-containing ligands, here thiourea by reaction 2, will break the thiocyanate bridges and give complexes where

$$[(CH_3)_2Au(SCN)]_{2(\text{hexane})} + 2SC(NH_2)_{2(aq)} \longrightarrow 2(CH_3)_2Au(SCN)(SC(NH_2)_2)(s) \quad (2)$$

both ligands are bound by sulfur. The product of reaction 2 is insoluble in water and most organic solvents, but the low melting point, 83°, is in accord with a molecular compound.

The di-μ-thiocyanato-*N,S* structure would be expected to be quite stable with the heavy d^8 transition metals. A bridge with 90° angles at the metal, 180° for M–N–C, and 90° for C–S–M should be unstrained. In addition to the gold(III) and platinum(II) complexes discussed here, it is very likely that the binuclear rhodium(I) complex $[Rh\{(p\text{-}C_6H_4CH_3O)_3P\}_2(SCN)]_2$ has a similar bridge. This compound was first reported by Vallarino,[37] who suggested bridging by the sulfur atoms alone. The reported infrared spectrum has a band at 2150 cm^{-1} consistent with the Au(III) and Pt(II) compounds.

Although the chemistries of $(CH_3)_2Au^{III}$ and $(CH_3)_2Ga^{III}$ are similar in a number of ways,[38] Dehnicke has found that dimethylgallium thiocyanate is a trimer and has assigned a structure with only sulfur bridging on the basis of the infrared spectrum.[39] This structure is not surprising, since bridging *via* both the nitrogen and sulfur ends of the thiocyanates would produce considerable strain with a tetrahedrally coordinated representative element.

The very low intensity of the Au–C stretching and C–Au–C bending vibrations in the infrared spectra of all of these compounds suggests that the Au–C bond moments are very small. This is consistent with the inertness of these bonds to attack by both electrophiles and nucleophiles.

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[35] M. E. Foss and C. S. Gibson, *J. Chem. Soc.*, 3074 (1949).

[36] Recently we have found that pyridine will cleave this bridge: G. C. Stocco and R. S. Tobias, unpublished research.

[37] L. Vallarino, *J. Chem. Soc.*, 2473 (1957).

[38] Compare, for example, the behavior in aqueous solution given by ref 6 and L. Pellerito and R. S. Tobias, *Inorg. Chem.*, **9**, 953 (1970).

[39] K. Dehnicke, *Angew. Chem.*, **79**, 942 (1967).

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The Interconversion of the *trans*-Dibromo- and *trans*-Dichlorodicyanoaurate(III) Anions[1]

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The replacement of the two bromide ligands in *trans*-$Au(CN)_2Br_2^-$ by chloride has been characterized as a stepwise process involving the intermediate *trans*-$Au(CN)_2ClBr^-$ complex. The kinetics of the first and second bromide replacements were studied by stopped-flow spectrophotometry, and both are found to obey two-term rate laws containing first- and second-order terms. Rate constants at 25° and $\mu = 0.51$ *M* for the first replacement are $k_1 = 2.1$ sec^{-1} and $k_2 = 1670$ M^{-1} sec^{-1}, while those for the second are $k_1 = 2.3$ sec^{-1} and $k_2 = 143$ M^{-1} sec^{-1}. Equilibrium measurements are reported and the synthesis of *trans*-$Au(CN)_2ClBr^-$ is described.

Introduction

Ligand replacement reactions of square-planar gold(III) complexes are generally rapid in aqueous solution—considerably more so than those of isostructural and isoelectronic platinum(II) complexes.[2] This feature has been one of the chief deterrents to their systematic investigation. Even though a number of replacement reactions of gold(III) have been studied in

[1] Presented at the Fourth Great Lakes Regional Meeting of the American Chemical Society, Fargo, N. D., 1970.

[2] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 410–414.