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Organogold(III) Complexes. Structure of Monomethyldibromogold

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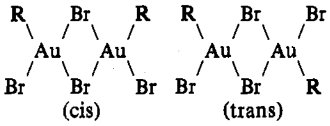
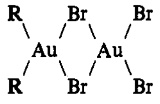
Organogold complexes[1] are valuable probes for the study of reductive elimination of organometallic intermediates in catalytic reactions.[2] Thus, trimethyl- and dimethyl(anionо)gold complexes with the formulations $(CH_3)_3AuL$ and $(CH_3)_2XAuL$, respectively [L = phosphines], afford only the homonuclear CH_3–CH_3 on reductive elimination.[1,3] We sought to examine the heteronuclear elimination of CH_3–X from the corresponding monomethyl analogues, $CH_3(X)_2AuL$. However, despite a number of efforts to synthesize such monoalkylgold(III) complexes, there are no unambiguous examples extant,[4] and it is generally concluded that they are unstable.[6,7] Attempts to prepare monoalkyldibromogold by electrophilic brominolysis of the dimeric dialkylbromogold according to eq 1 indeed led to compound I [R = ethyl, *n*-propyl] with the correct empirical formula.[6] Although it was recognized that two structures, the symmetric II (trans and cis) as well as the unsymmetric III, were possible, they could not be distinguished on the basis of chemical studies and dipole measurements.[6] Since these efforts represent a potentially valuable route to the desired monoalkylgold(III) complexes, we examined the structure of the methyl analogue of I in detail.

$$[R_2AuBr]_2 + 2Br_2 \rightarrow \underset{\text{I}}{[RAuBr_2]_2} + 2RBr \qquad (1)$$



II



III

Experimental Section

Materials. The gold complexes, $[(CH_3)_2AuBr]_2$, $(CH_3)_2XAuPPh_3$ [X = Br, I], $BrAuPPh_3$, CH_3AuPPh_3, were prepared using published procedures.[3,8] The halogenophospines, $X^-XPPh_3^+$ [X = Br, I], were synthesized from X_2 and PPh_3.[9] A colorless solution of $[(CH_3)_2AuBr]_2$ (25.0 mg) in CCl_4 (1.0 ml) was treated with bromine (5.5 μL) to give a red solution which gradually deepened and then lightened on standing for 3 days at room temperature as dark red crystals of IV separated from solution. During this change the singlet (δ 1.40) in the ^1H NMR spectrum of $[(CH_3)_2AuBr]_2$ decreased concomitantly with an increase in that due to CH_3Br (δ 2.55) which was finally formed in 75% yield. The solution on further standing at room temperature gradually evolved ethane. Compound IV forms transparent dark red crystals when freshly prepared, but gradually changes in solution or in the solid state to an opaque black solid within a week. All ^1H NMR spectra were recorded on a Varian EM360 spectrometer using external TMS standards.

X-Ray Crystallographic Study of IV. A crystal of dimensions 0.70 × 0.078 × 0.064 mm was placed in a gaseous nitrogen cold stream on the goniostat and maintained at −160 ± 5 °C throughout characterization and data collection. The diffractometer used consisted of a Picker four-circle goniostat with a graphite monochromator (002 plane), and a Texas Instruments T1980B minicomputer. The goniostat was controlled by stepping motors using locally designed interfaces and programs.

The crystal was characterized on the goniostat and found to be $C2/c$ with $a = 12.202$ (2) Å, $b = 10.722$ (2) Å, $c = 7.673$ (2) Å, and $\beta = 94.19\ (1)^\circ$ at −160 °C as determined by a least-squares fit of angular data from 12 centered reflections. The calculated density for $Z = 4$ is 4.93 g/cm^3. Redundant intensity data were collected by 2θ scan techniques (4°/min) to a maximum of $2\theta = 55^\circ$. The intensity data were reduced in the usual manner,[10] corrected for Lorentz–polarization terms and absorption (μ 449.3 for λ(Mo Kα) 0.71069 Å), and reduced to the 1152 unique structure amplitudes. The 1125 structure amplitudes with $F_o^2 > \sigma(F_o^2)$ were considered "observed" and used in all calculations. An ignorance factor of 0.06 was used in the data reduction formula.

The structure, which possesses crystallographic twofold symmetry, was solved by a combination of direct and Patterson techniques and refined anisotropically by full-matrix least-squares.[11] The function minimized was $\sum w(|F_o| - |F_c|)^2$ in which w is $4F_o^2/\sigma^2(F_o^2)$. The final residuals were $R(F) = 0.058$ and $R_w(F) = 0.050$, where $R(F)$ and $R_w(F)$ are defined as $\sum||F_o| - |F_c||/\sum|F_o|$ and $[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. The "goodness of fit" for the last cycle was 1.68, and the largest Δ/σ was 0.03. A final difference Fourier synthesis was featureless except for peaks of 2.2 and 2.1 e/Å^3 remaining in the location of the gold atoms.

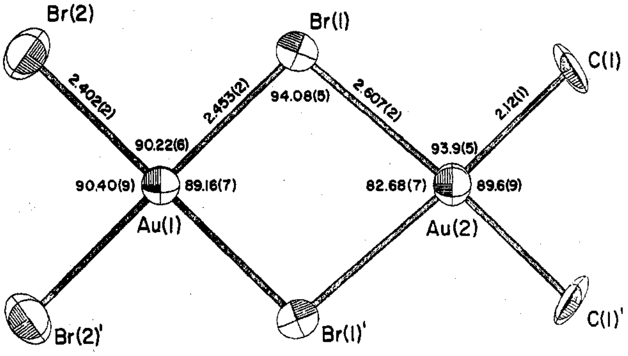


Figure 1. ORTEP drawing of the molecule showing bonded distances and angles. Primed atoms are related to nonprimed atoms by a twofold axis which passes through the two gold atoms. Thermal ellipsoids are drawn at the 50% probability level. The gold–gold distance is 3.705 (1) Å, where the number in parentheses represents the error in the least significant digits.

Results and Discussion

Treatment of dimethylbromogold with an equimolar amount of bromine in carbon tetrachloride solution at room temperature afforded high yields of methyl bromide, and methyldibromogold (IV) separated from solution as dark red crystals according to eq 2.

$$[(CH_3)_2BrAu]_2 + 2Br_2 \rightarrow \underset{\text{IV}}{2CH_3(Br_2)Au} + 2CH_3Br \qquad (2)$$

To avoid decomposition, the diffraction data were collected on a freshly prepared transparent crystal of IV held at −160 °C. The molecular structure of IV in Figure 1 is planar and consists of discrete dimeric units of two gold atoms, each in a square-planar configuration and held with two bridging bromine atoms. Importantly, both methyl groups in the dimer are bonded to the same gold atom. The bond distances and bond angles in Figure 1 and Table I are comparable to those found in the binuclear structure in $[(CH_3CH_2)_2AuBr]_2$.[12]

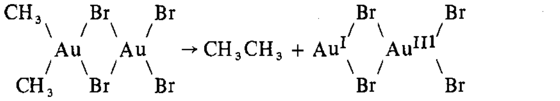
Table I. Fractional Coordinates and Thermal Parameters for $Au_2Br_4(CH_3)_2$

Atom	x	y	z
Au(1)	0.000 00[a]	0.918 42 (7)	0.250 00[a]
Au(2)	0.000 00[a]	0.263 96 (8)	0.250 00[a]
Br(1)	0.132 10 (12)	0.081 40 (14)	0.345 81 (22)
Br(2)	0.368 86 (14)	0.260 54 (16)	0.156 66 (25)
C(1)	0.112 4 (13)	0.404 2 (13)	0.341 4 (23)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Au(1)	0.003 35 (5)	0.004 25 (7)	0.010 32 (15)	0.000 00[a]	0.000 35 (7)	0.000 00[a]
Au(2)	0.003 82 (6)	0.004 13 (7)	0.012 51 (18)	0.000 00[a]	0.000 81 (8)	0.000 00[a]
Br(1)	0.003 73 (10)	0.005 20 (13)	0.015 43 (32)	−0.000 30 (9)	−0.001 07 (14)	−0.000 31 (16)
Br(2)	0.005 52 (12)	0.006 14 (16)	0.019 69 (39)	−0.001 59 (10)	0.000 96 (17)	−0.002 57 (19)
C(1)	0.005 5 (11)	0.003 5 (13)	0.017 2 (33)	−0.002 6 (9)	0.000 3 (15)	−0.000 38 (17)

[a] Parameters fixed by symmetry. The form of the anisotropic thermal parameter is: $\exp[-(h^2b_{11} + \ldots + 2hkb_{12} + \ldots)]$.

Methyldibromogold (IV) is thus a mixed binuclear species with the general structure III, in which one gold moiety consists of dimethylbromogold(III) and the other is tribromogold(III).[13] In accord with structure III, reductive elimination at 70 °C for 3 days produced ethane in high yields (and only traces of methyl bromide), together with a black opaque solid, which we formulate as $AuBrAuBr_3$ (eq 3) since



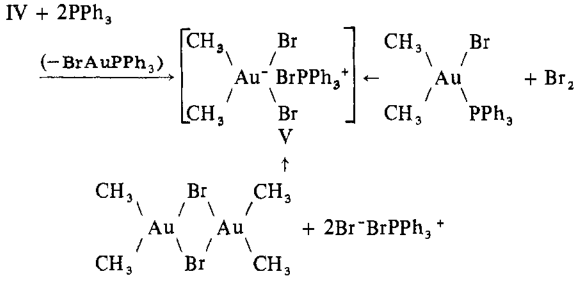
IV

(3)

it affords bromine and aurous bromide (AuBr) on further heating above 200 °C.[14]

The complex IV is sparingly soluble in chloroform [^1H NMR: $AuCH_3$ δ 1.60 ppm (singlet)]. When the purple solution is treated with 2 equiv of triphenylphosphine, the expected ^1H NMR spectrum [cis CH_3 δ 1.03, J_{HP} = 8 Hz; trans CH_3 δ 1.50, J_{HP} = 9 Hz] due to the known[3] $(CH_3)_2BrAuPPh_3$ could not be detected, but only a singlet at 1.3 ppm was observed. The $^{31}P\{^1H\}$ NMR spectrum showed two singlets in a 1:1 ratio at 52.0 and 35.6 ppm relative to external H_3PO_4. The resonance at 52.0 ppm is assigned to $BrPPh_3^+$ by comparison with an authenic sample of $Br^-BrPPh_3^+$ (51.9 ppm) and that at 35.6 ppm is assigned to $BrAuPPh_3$.

When a colorless solution of *cis*-$(CH_3)_2BrAuPPh_3$ in $CDCl_3$ was treated with a stoichiometric amount of bromine, no methyl bromide was observed, and the ^1H NMR spectrum (δ 1.3 singlet) and $^{31}P\{^1H\}$ NMR spectrum (δ 51.3 singlet) of the yellow solution indicated that the same species as that described above was formed. Similarly, the singlet resonance in the ^1H NMR spectrum of $[(CH_3)_2AuBr]_2$ in $CDCl_3$ was shifted from 1.40 ppm to 1.30 ppm when an equimolar amount of $Br^-BrPPh_3^+$ was added. Since cleavage of a CH_3–Au bond does not occur and the NMR spectra are common, we propose the formation of the same dimethylgold(III) species, V,[15] in all three reactions described above.



The singular absence of any stable monomethylgold(III) species in these studies[16] suggests that they are less stable than the dimethylgold(III) precursors. This conclusion is supported by the failure to oxidize the methylgold(I) complex, CH_3AuPPh_3, by iodine to a monomethyliodogold(III) species according to

$$CH_3Au^IPPh_3 + I_2 \rightarrow CH_3(I)_2Au^{III}PPh_3 \qquad (4)$$

Instead, the ^1H NMR spectrum of the $CDCl_3$ solution indicated the presence of a mixture of the known $(CH_3)_2IAuPPh_3$ [δ 1.20, J_{PH} = 8 Hz; δ 1.67, J_{PH} = 9 Hz] together with CH_3I [δ 2.23 (s)] and $(CH_3)_2AuI_2^-IPPh_3^+$ [δ 1.60 (s)].[17] The latter can also be isolated as a red oil from benzene when $(CH_3)_2IAuPPh_3$ is treated with iodine, and on standing it liberates CH_3–CH_3 by reductive elimination.

Acknowledgment. We wish to thank the National Science Foundation for financial support and Mr. Kevin Rollick for the ^{31}P NMR spectra.

Registry No. IV, 61886-04-2; V, 61886-07-5; $[(CH_3)_2AuBr]_2$, 30626-28-9; *cis*-$(CH_3)_2BrAuPPh_3$, 34275-47-3; $(CH_3)_2IAuPPh_3$, 34275-48-4; $(CH_3)_2AuI_2^-IPPh_3^+$, 61886-06-4.

Supplementary Material Available: Tables listing structure factor amplitudes and atomic parameters for compound IV (11 pages). Ordering information is given on any current masthead page.

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(13) Structure III for alkyldibromogold complexes also explains their ready reducibility in contrast to the dialkylbromogold analogues (see ref 6b and 6d).

(14) (a) Cf. F. Ephraim, *Chem. Ber.*, **52**, 241 (1919), and J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 3, Longmans, Green and Co., London, 1923, p 606. (b) On the other hand, reductive elimination of the ethyl analogue was reported to produce ethyl bromide which was inferred from the weight loss.[6b]

(15) (a) V is written as an ion pair in analogy to Br^- $BrPPh_3^+$ [see ref 9]. (b) Stable salts of dimethyldihaloaurate(III) [^{1}H NMR of $Ph_4As^+ \cdot (CH_3)_2AuBr_2^-$: δ 1.21]. W. M. Scovell and R. S. Tobias, *Inorg. Chem.*, **9**, 945 (1970); see also G. C. Stocco and R. S. Tobias, *J. Am. Chem. Soc.*, **93**, 5057 (1971).

(16) Compound IV may be formed from I in eq 2 directly by brominolysis of two methyl groups on the same gold atom. Alternatively, cleavage of two methyl groups on separate gold atoms in I could afford a metastable monomethyldibromogold dimer (i.e., II cis or trans) which then rearranges to IV.

(17) (a) The ^{1}H NMR spectrum of $Ph_4As^+(CH_3)_2AuI_2^-$ shows the methyl singlet at δ 1.45 ppm [see ref 15b]. (b) A methylgold(III) species presented in eq 4 may be an intermediate in the formation of dimethylgold(III) complexes since methyl transfer from CH_3AuPPh_3 can be facile,[18] e.g., $CH_3I_2AuPPh_3 + CH_3AuPPh_3 \rightarrow (CH_3)_2IAuPPh_3 + IAuPPh_3$, etc.

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Uranium(IV) Sulfite and Uranium(IV) Oxysulfite

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Efforts to prepare sulfites of uranium have led to products of indefinite composition or have employed conditions that prevented the isolation of sulfites of uranium(IV). Rosenheim and Kelmy[1] reported the isolation of $(NH_4)_4[U(SO_3)_4]$ but this could not be confirmed during the present studies. Other early efforts to isolate sulfites of uranium(VI) demonstrated their existence in solutions from which only products of irreproducible composition could be isolated.[2,3] Both Aloy and Auber[4] and Yevteev and Petrzhak[5] reduced uranyl salts with sodium dithionite and sodium formaldehyde sulfoxylate, respectively, but reoxidized the products to sulfates by recrystallization from sulfuric acid.

There are several cases in connection with the processing of uranium ores in which uranium(IV) sulfite was probably formed but not isolated because of the conditions employed.[6-8] In a similar context precipitation of uranium(IV) sulfite was precluded by the presence of fluoride ion[9,10] and the preferential separation of $(NH_4)UF_5$. Other related actinide chemistry is concerned with sulfite complexes of neptunium(V)[11] and with the use of sodium dithionite for the reduction of higher oxidation states of plutonium to plutonium(III).[12]

We report here the synthesis of uranium(IV) sulfite as the tetrahydrate, its characterization, and pyrolysis to high purity uranium(IV) oxide. Also included is a closely related product, uranium(IV) oxysulfite–4-water.

Experimental Section

All experimental methods and physical measurements were made as described earlier.[13] For cases in which, for example, x-ray diffraction, spectral, DTA, or TGA data are given here only in part, the complete data are available elsewhere.[14]

Uranium(IV) Sulfate–4-Water. In a typical experiment, a solution of 3.3780 g of $Na_2S_2O_4$ (2.5-fold in excess of a 1:1 mol ratio) in 100 ml of water was added with stirring to 3.7816 g of $UO_2(NO_3)_2 \cdot 6H_2O$ in 100 ml of water. From the resulting deep red solution, a pale green precipitate separated immediately. After 10 min of stirring, the precipitate was filtered in an atmosphere of nitrogen and washed with six 50-ml portions of water. The product was then washed with three 25-ml portions of ethanol and dried by drawing dry nitrogen through the filter cake. Anal. Calcd for $U(SO_3)_2 \cdot 4H_2O$: U, 50.64; S, 13.62; H, 1.70. Found: U, 50.73; S, 13.66; H, 1.76. X-ray diffraction data (*d* spacings in Å; relative intensities in parentheses): 6.60 (1.0), 4.10 (0.8), 3.99 (0.8), 3.83 (0.7), 3.31 (0.5), 2.18 (0.5). Crystallite size, 0.0400 μm. The yield was essentially quantitative.

A 0.0024-g sample of $U(SO_3)_2 \cdot 4H_2O$ was placed in a furnace preheated to 650 °C in a dry nitrogen atmosphere and heated for 75 min. After cooling to 25 °C, the sample was found to have lost 0.0475 g or 42.26% of the original weight. The weight loss calculated for the elimination of $4H_2O$ and $2SO_2$ is 42.55%. Anal. Calcd for UO_2: U, 88.15. Found: U, 88.36; S, 0.02; Na, 0.07. X-ray diffraction data: 3.13 (1.0), 2.71 (0.5), 1.92 (0.6), 1.64 (0.5). Crystallite size, 0.4270 μm.

Uranium(IV) Oxysulfite–4-Water. When the foregoing procedure for the synthesis of $U(SO_3)_2 \cdot 4H_2O$ was changed *only* to the extent of conducting the filtration without protection from exposure to the atmosphere, the color of the precipitate changed from pale green to dark gray; this product was washed and dried as described above. The yield was quantitative; the product did not give an x-ray diffraction pattern. Anal. Calcd for $UO(SO_3) \cdot 4H_2O$: U, 58.62. Found: U, 58.36. When this product was dried at 10^{-2} Torr over P_2O_5 for 12 h, the color changed from dark gray to light gray. Anal. Calcd for $UO(SO_3) \cdot 2H_2O$: U, 64.32; S, 8.65; H, 1.08. Found: U, 64.16; S, 8.65; H, 1.15; Na, 0.36 ppm. This product also did not give an x-ray diffraction pattern.

A 7.394-mg sample of the tetrahydrate was heated to 218 °C under dry nitrogen in a DTA sample holder. After cooling to 25 °C the weight loss was found to be 1.317 mg or 17.81%; that required for the loss of $4H_2O$ is 17.73%. A larger sample (0.7292 g) was heated in a furnace at 600 °C for 90 min; the weight loss found was 0.2451 g or 33.61% as compared with 33.50% calculated for the loss of $4H_2O$ and SO_2. Anal. Calcd for UO_2: U, 88.15. Found: U, 87.96; S, 0.01; Na, 0.13. X-ray diffraction data: 3.10 (1.0), 2.69 (0.5), 1.91 (0.5), 1.63 (0.5). Crystallite size, >0.5000 μm. When the decomposition was carried out at temperatures below 600 °C (e.g., at 550°) the x-ray diffraction pattern included *d* spacings attributable to UO_2 but also the following ones which are characteristic of UOS: 2.70 (0.4), 1.94 (1.0), 1.65 (0.8), 1.57 (0.4), 1.37 (0.2), 1.22 (0.3). Slower initial heating rates appeared to favor the formation of UOS.

Discussion

It should be emphasized at the outset that the synthesis of essentially pure $U(SO_3)_2 \cdot 4H_2O$ is accomplished only by rigorous exclusion of atmospheric oxygen during both filtration and washing. Thereafter it can be stored indefinitely without decomposition in an inert atmosphere. As shown by DTA and TGA data,[14] this salt is decomposed to UO_2 as follows. An endotherm at 75 °C corresponds to the loss of 3.08 mol of H_2O followed by a broad endotherm beginning at ca. 110 °C which coincides with the loss of 1.02 mol of H_2O. The decomposition of the anhydrous salt is characterized by three endotherms: 550 °C (−0.50 mol of SO_2), 590–680 °C (−0.98 mol of SO_2), and 690 °C (−0.52 mol of SO_2).

The pyrolysis of the product formulated above as $UO(SO_3) \cdot 4H_2O$ proceeded essentially the same as described above except for a sharp endotherm at 460 °C that corresponds to the loss of 0.93 mol of SO_2. In the case of the dihydrate, an endotherm at 90 °C corresponds to loss of 2.03 mol of H_2O; at higher temperatures the data were less conclusive. An endotherm at 690 °C corresponds to the loss of 2.03 mol of H_2O and correlates with a loss of 48 amu from the TGA data. Both results are compatible with the formation of UOS which, as noted above, was detected by x-ray diffraction data. Experiments conducted on a much larger scale, however, led to analytical data which showed that the oxysulfide was a minor component in all cases.

It should also be pointed out that the analytical data for $UO(SO_3) \cdot 2H_2O$ are equally compatible with the formulation $U(OH)_2(SO_3) \cdot H_2O$. The latter seems untenable, however, since it could arise only by hydrolysis of a dried salt that was formed in an aqueous medium. The product in question can be explained only on the basis of oxidation of the normal