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Dimethylgold(III) Complexes of α-Amino Acids and Related Ligands

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Dimethylgold(III) complexes with the anions of glycine, alanine, valine, cysteine, histidine and imidazole, benzimidazole and 1,2,4-triazole, respectively, have been prepared. The structures of the complexes are discussed on the basis of their infrared spectra.

As a continuation [1] of our studies on square planar α-amino acid complexes of platinum(II) [2] and on dimethylgold compounds [3] we have been interested in dimethylgold amino acidates. Until now only a few amino acid complexes of gold have been described [4]. Gold complexes have found intererest because of their ability to act as antiinflammatory agents [5].

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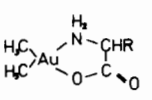
Colourless monomeric dimethylgold(III) complexes with the anions of α-amino acids as chelating ligands have been obtained by reaction of $[(H_3C)_2Au(OH_2)_2]NO_3$ with the sodium amino acidates in aqueous solution.



1

	R
1a	H
b	CH_3
c	$CH(CH_3)_2$

The gold complexes **1** decompose easily on exposure to light, especially in ethanolic solution, to give metallic gold. The νCO stretching bands of **1** at 1600 cm^{-1} (Table I) are characteristic of chelating aminoacidates [6]. Some dimethylgold complexes with other N and O bound chelate ligands, *e.g.* Schiff bases, have been reported [7].

TABLE I. Assignment of I.r. Absorption Bands (cm^{-1}) in KBr.[a]

Compound		νNH, νCH	δNH_2	$\nu_{as}C{=}O$	$\nu_{sym}C{=}O$	$\delta_s CH_3(Au)$
$(CH_3)_2Au(glyO)$	**1a**	3211 m, 3118 m, 2980 m–w, 2930 sh, 2910 m	1620 s	1602 s,b	1370 m–s, 1382 sh	1246 m, 1208 m
$(CH_3)_2Au(alaO)$	**1b**	3260 sh, 3214 m, 3102 m, 2975 m, 2915 m	1644 m	1607 s,b	1372 m–s, 1390 sh	1242 m, 1205 m
$(CH_3)_2Au(valO)$	**1c**	3241 m, 3129 m, 2962 m, 2907 m, 2875 w, 2810 w	1655 sh	1628 s,b	1370 sh, 1385 m–s, 1395 sh	1244 m, 1210 m
$(CH_3)_2Au(cysO)$	**2**	3210 w, 3110 w, 3000 m–w, 2910 w	1710 m-w	1625 s,b	1390 sh, 1382 m–s	1217 m, 1187 m
Au(hisO)•hisOH	**3**	3210 w, 3130 w, 3000 w, 2910 w	1655 sh	1625 s,b	1400 sh, 1380 m–s, 1365 sh	–

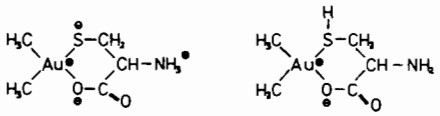
[a]I.r. spectra were recorded with a Perkin-Elmer 325 instrument.

TABLE II. Elemental Analyses.

Compound		C%		H%		N%		Au%		Dec. p. °C
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
$(CH_3)_2Au(glyO)$	**1a**	15.98	16.52	3.34	3.33	4.65	4.56	–	–	128
$(CH_3)_2Au(alaO)$	**1b**	19.67	19.06	3.79	3.84	4.46	4.45[a]	–	–	–
$(CH_3)_2Au(valO)$	**1c**	24.50	25.19	4.70	4.67	4.08	4.37	–	–	165
$(CH_3)_2Au(cysO)\cdot H_2O$	**2**	16.44	16.64	3.31	3.45	3.84	3.79	–	–	170
$Au(HisO)\cdot HisOH\cdot 2H_2O$	**3**	26.58	25.88	3.90	3.95	15.50	15.65	–	–	–
$(CH_3)_2Au(Imidazolate)$	**4a**	20.4	20.3	3.09	2.89	9.53	9.78	67.0	66.6	183–4
$(CH_3)_2Au(Benzimidazolate)$	**4b**	31.4	31.6	3.23	3.45	8.14	8.26	57.2	57.2	222–4
$(CH_3)_2Au(1,2,4triazolate)$	**4c**	16.3	16.2	2.74	2.54	14.2	14.0	66.7	66.6	206–9
$(CH_3)_2AuCl(1\text{-}MeImidazole)$	**5**	20.9	21.2	3.52	3.55	8.13	8.29	57.2	56.6[b]	101–2

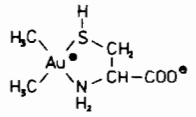
[a]Molecular weight: Calc. 315.1, Found 329, osmometrically in $CHCl_3$. [b]Cl% Calc. 10.3, Found 10.2.

Cysteinate also forms a 1:1 complex with dimethylgold(III). For this complex **2** six different structures have to be discussed.

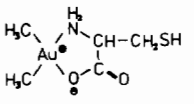


2a

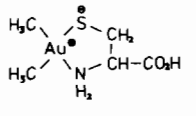
2b



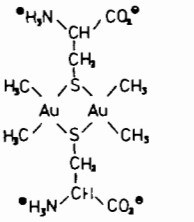
2c



2d



2e



2f

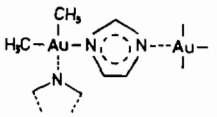
Cysteinato chelate complexes are known to coordinate either through O and S or N and S, respectively [8].

The ir data of **2** show that structure **2a** with S and O chelation is present. The same type of S- and O-bound cysteinate has been suggested on the basis of ir data for cysteinato complexes of Pd(II) and Pt(II) [9]. In the ir spectrum of **2**, the ν(SH) stretching band is absent; although the intensity of an νSH stretching band may be weak, there is no indication of an absorption in the region 2000–2700 cm^{-1}. Thus the structures 2b, c and d can be excluded. This is also consistent with Raman studies of aqueous solutions containing equimolar $[(CH_3)_2Au(OH_2)_2]NO_3$ and disodium mercaptosuccinate. The $Na_2[O_2CCH(SH)CH_2CO_2]$ has a moderately intense ν(SH) at 2577 cm^{-1} which was observed at 2578 cm^{-1} with mercaptosuccinic acid. The aqueous solution containing dimethylgold(III) exhibited no measurable scattering in the 2000–2800 cm^{-1} region. Mercaptides are very good ligands for organogold(III) cations, and with mercaptosuccinate a highly soluble complex is formed. The very intense and broad band of **2** at 1625 cm^{-1} which remains unchanged on deuteration of **2** with D_2O indicates the presence of a unidentate carboxylate group, COO^-. The ir data of **2** are quite different from that of palladium and platinum complexes which contain N and S coordinated methionine with the free carboxylic group [10] and which exhibit rather sharp ν_{as} COOH absorptions at higher wavenumbers (~1720 cm^{-1}). The broad and intense νNH band of **2** at 3000 cm^{-1} with peaks at 2910, 3000, 3130, 3210 cm^{-1} disappears on deuteration.

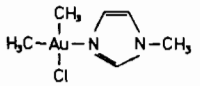
Reaction of $[(H_3C)_2Au(OH_2)_2]NO_3$ with methionine and serine in aqueous solution gave only precipitation of metallic gold. A complex of analytical composition [Au(histidinate)(histidine)], **3**, resulted from the reaction of $[(H_3C)_2Au(OH_2)_2]NO_3$ with histidine. In the ir spectrum of **3**, the $\delta_s(CH_3)$ bands are absent; thus reductive elimination of methyl groups [11] must have occurred.

Raman spectroscopic studies on aqueous solutions of $[(CH_3)_2Au(OH_2)_2]^+$ and imidazole-like ligands have shown that in neutral aqueous solution coordination occurs at the pyrrole type nitrogens with substitution for the proton [15]. Consistent with this is the isolation of colourless compounds **4** a–c by reaction of $[(CH_3)_2AuOH]_4$ with imidazole, benzimidazole, and 1,2,4-triazole. The low solubility of these compounds is consistent with a polymeric

structure where the imidazole bridges through the 1 and 3 positions. Similar compounds have been prepared with $(CH_3)_2Tl(III)$ and Tl(I) [16]. With 1-methylimidazole, where ligand deprotonation is



blocked, 5 can be obtained by a bridge splitting reaction of $[(CH_3)_2AuCl]_2$ with 1-methylimidazole.



5

In the reaction with histidine, it is likely that $[(CH_3)_2Au$(histidinate)] is formed initially. Although either the carboxylate or amino groups can coordinate when imidazole is deprotonated [17], neither of these is a particularly good ligand for $(CH_3)_2Au(III)$. Similar dimethylgold(III) compounds with one good and one weak donor have been observed to be highly unstable to reductive elimination of ethane [3], because these processes all appear to be dissociative. Consequently, reductive elimination from $(CH_3)_2Au$-(histidinate) occurs, and additional histidine traps the Au(I) product.

Experimental

*α-Aminoacidatodimethylgold(III) (**1**a–c)*

To a solution of $[(H_3C)_2AuI]_2$ [12] (715 mg, 1.0 mmol) in petroleum ether (20 ml) was added a solution of $AgNO_3$ (360 mg, 2.1 mmol) in water (30 ml). With stirring, the organic solvent was removed *in vacuo* and the precipitate of AgI was filtered off. To the aqueous solution of $[(H_3C)_2Au(OH_2)_2]NO_3$ was added a solution of the sodium amino acidate [13] (2 mmol) in water (5 ml). After standing for 0.5 h (25 °C), the solution was evaporated to dryness, and the residue was dissolved in ethanol. From the filtered solution the complexes were precipitated by adding diethyl ether.

*Cysteinatodimethylgold(III) (**2**)*

To a solution of $[(H_3C)_2Au(en)]I$ [14] (500 mg, 1.21 mmol) in water (20 ml) was added concentrated hydrochloric acid (1.5 ml). The white precipitate was extracted with three portions of petroleum ether (7 ml). To the petroleum solution was added a solution of $AgNO_3$ (213 mg, 1.25 mmol) in water (20 ml). The organic solvent was removed *in vacuo* and the precipitate of AgI was filtered off. To the aqueous solution was added a solution of cysteine (152 mg, 1.25 mmol) in water (7 ml). After stirring, a white precipitate was obtained which was washed with ether and recrystallized from methanol/diethyl ether. Colorless crystals (60% yield). The molecular weight could not be measured due to the insolubility of the compound. It was also not possible to obtain a mass spectrum of the undecomposed complex.

*Histidinatogold(I) (**3**)*

This complex was obtained similarly as described for **2**, using 500 mg $[(H_3C)_2Au(en)]I$ and 194 mg (1.25 mmol) histidine. This complex did not precipitate from its aqueous solution. Therefore the solution was evaporated to dryness and the residue was recrystallized from methanol/diethylether.

*Imidazolatodimethylgold(III) (**4a**)*

To a solution of excess imidazole in diethyl ether was added $[(CH_3)_2AuOH]_4$ [14] (0.2023 g, 0.829 mmol based on monomer). The mixture was stirred for 30 min by which time the granular hydroxide no longer could be seen in the fluffy white precipitate which formed. This was collected on a frit and dried under vacuum over P_4O_{10} at 5 °C. Yield: 0.2009 g, 82.4%.

*Benzimidazolatodimethylgold(III) (**4b**)*

To a solution of benzimidazole (0.1115 g, 0.945 mmol) in 20 ml absolute ethanol was added $[(CH_3)_2$-$AuOH]_4$ (0.1015 g, 0.416 mmol of monomer). The mixture was stirred one hour, filtered, and the precipitate was dried under vacuum over P_4O_{10} at 5 °C. Yield: 0.1265 g, 88.4%.

*1,2,4-Triazolatodimethylgold(III) (**4c**)*

To a solution of 1,2,4-triazole (0.0869 g, 1.26 mmol) in 20 ml absolute ethanol was added $[(CH_3)_2$-$AuOH]_4$ (0.0967 g, 0.396 mmol monomer). After stirring for one hour, the mixture was filtered and the precipitate was dried under vacuum over P_4O_{10} at 5 °C. Yield: 0.0758 g, 64.9%.

*Chloro(1-methylimidazole)dimethylgold(III) (**5**)*

To a solution of $[(CH_3)_2AuCl]_2$ [18] (0.1528 g, 0.583 mmol of monomer) in 10 ml cyclopentane was added a stoichiometric amount of 1-methylimidazole (0.0479 g, *ca.* 30 μl) with a microliter syringe. The white precipitate which formed immediately was collected on a frit and dried under vacuum over P_4-O_{10} at 5 °C. Yield: 0.1275 g, 63.6%.

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